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EVALUATION OF THE ADHESIVE BONDING PROCESSES USED IN HELICOPTER MANUFACTURE. PART 7. PREPRODUCTION EVALUATION OF IMPROVED TITANIUM SURFACES PREPARATION

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Prepared for:

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OBJECT

To evaluate various parameters of the PHOSPHATE-FLUORIDE TREATMENT (STABILIZED) surface preparation process for titanium.

ABSTRACT

The PHOSPHATE-FLUORIDE TREATMENT (STABILIZED) has been compared directly to a standard Phosphate-Fluoride Treatment for the surface preparation of commercially pure titanium sheet. The stabilized treatment process was found to provide an improvement in the durability of adhesive bonded joints exposed to moisture and stress. The treatment processes were compared for their effect on the properties of the basis metal as well as for bondability and durability. Laboratory evaluations included standard specification qualification testing as well as special durability tests.

CONCLUSIONS

The Stabilized Phosphate-Fluoride treatment process:

- Does not degrade commercially pure titanium sheet beyond acceptable limits.
- Produces bond strengths, with the adhesives tested, which are equivalent to those produced by the standard phosphate-fluoride treatment.
- Produces bonded joints which are less susceptible to moisture penetration than those produced by the standard treatment.
- Improves the durability of bonded joints exposed to wet cyclic creep testing.
- Is recommended for use as a surface preparation for titanium which is to be adhesive bonded.
- Should be evaluated further to determine the effects of higher sulfate concentrations, i.e. 5-8 oz/gal range.
- Should receive additional study in the area of process control analysis procedures and sulfate concentration control.

INTRODUCTION

The object of this program was to evaluate various parameters of the PHOSPHATE-FLUORIDE TREATMENT (STABILIZED) surface preparation process for titanium to establish the operational control procedures necessary for scale-up to production size, to conduct confirming laboratory qualification tests and to provide other data which may be used to determine the suitability of the process for use in the production of adhesive bonded titanium structures.

This process, developed by Picatinny Arsenal (Reference 1), is a modification of the PHOSPHATE FLUORIDE TREATMENT specified in MIL-A-9067 for use as a surface preparation for titanium prior to adhesive bonding.

Initially, titanium surfaces were prepared for adhesive bonding by alkaline cleaning, nitric-hydrofluoric acid pickling, and/or anodic treatments. These treatments provided good immediate bond strengths with most adhesives. However, the durability of the bonded joints was marginal to poor (Reference 2). As a result of the poor resistance to service environments, the PHOSPHATE-FLUORIDE TREATMENT was put into use.

The PHOSPHATE-FLUORIDE TREATMENT provides a surface which produces both good immediate bond strengths and increases the resistance of the bonded joint to deterioration from environmental exposure. However, the durability of the bonded joints was proven to be less than optimum.

Hamilton (Reference 3), in his studies to characterize the adherend surface, has found that the durability of the bonded joint is dependent on the structure of the oxide on the titanium surface. Titanium dioxide occurs in several forms - two of which are anatase and rutile. Although both forms of the oxide are stable in bulk, in thin films such as those found on the surface of a metal sheet, conversion from anatase to rutile can occur during exposure to some enviroments. The change in physical structure from anatase to rutile is accompanied by a volume change of approximately eight percent. This change could produce extremely high stresses at the adhesive-oxide interface.

The alkaline cleaning process produced a surface which was predominately rutile. The phosphate-fluoride treatment, on the other hand, produces an anatase surface which appears to provide a more permanent bond. However, the anatase is reported to convert to rutile upon exposure to air and/or in the bond joint (Reference 3).

The PHOSPHATE-FLUORIDE TREATMENT (STABILIZED) appears to produce a stable anatase surface coating which will provide both good immediate bond strengths and improved durability (Reference 1). Therefore, this program was established to provide a direct comparison of the STABILIZED TREATMENT process to a standard phosphate-fluoride treatment process.

DISCUSSION AND RESULTS

EXPERIMENTAL

The basic requirements for a surface preparation process for structural adhesive bonding are (1) the process must produce good durable bonded joints, (2) the process must not degrade the adherend material properties, and (3) the process must be controllable and provide repeatable results.

The experimental program was established with the above requirements in mind. The first studies included an evaluation of procedures for analysis of the various solutions and the effect of solution concentrations on base metal properties. The bondability of prepared surfaces and the durability of bonded joints were then determined. The final phase of the program consisted of manufacturing and testing of a production bonded panel.

Insofar as was possible, each test was designed to provide a direct comparison of surfaces treated by the standard phosphate-fluoride treatment process to those treated by the modified phosphate-fluoride process.

MATERIALS USED

Titanium Sheet - All bonding tests were accomplished with titanium sheet conforming to MIL-T-9046, Type I, Composition B, C.P. (Commercially Pure).

Chemicals - Technical grade chemicals were used in the preparation of all processing solutions except as noted in the body of this report.

Water - Deionized (D.I.) water was used to prepare all processing solutions. The water was produced by double bed ion exchange units and is controlled within the following limits (Reference 4):

Minimum of 50,000 ohm/cm resistance at 30°C
Phenolphthalein alkalinity of not more than 1 ppm.
Total alkalinity of not more than 10 ppm.
Chloride content of not more than 15 ppm.

Adhesives - Four adhesive systems were used:

AF126-2 Film Adhesive EC3909 Primer	3M Company AC&S Division
N227 Film Adhesive N2271A Primer	Whittaker Corp. Narmco Materials Div.
EA9605 Film Adhesive	Dexter Corp. Hysol Division
FM98 Film Adhesive	American Cyanimid Bloomingdale Division

The adhesives selected for this evaluation include two which have a relatively high metal-to-metal peel strength (AF126 and N227) and two which have an inherently low peel strength (FM98 and EA9605). The FM98 and EA9605 are designed to maintain a high shear strength level at elevated temperature. The bondability test results show the lap shear strength at 180°F to be higher than at ambient temperature (75°F). Metal-to-metal peel tests were run with these two adhesives to determine if a cohesive versus adhesive failure mechanism could be detected in the exposure tests.

These four adhesives were selected because they are being used currently and/or have been used recently in the manufacture of adhesive bonded panels for helicopter construction.

Titanium Surface Treatments

The PHOSPHATE-FLUORIDE TREATMENT (MIL-A-9067 and Bell Process Specification 4352) is accomplished by the following steps:

1. Degrease - Solvent Clean
2. Alkaline Clean - Nonsilicated cleaner - 5%-10% Vol., 120-130°F 5-15 minutes
3. Rinse - D.I. Water
4. Acid Pickle - See below*
5. Rinse - D.I. Water
6. Phosphate-Fluoride Treatment:
   Trisodium Phosphate 6.5-7.5 oz/gal
   Potassium Fluoride 2.5-3.0 oz/gal
   Hydrofluoric Acid (70%) 2.2-2.5 fl oz/gal
   room temperature for 2 minutes
7. Rinse - D.I. Water
8. Hot Water Soak - D.I. Water 145-155°F 14-16 minutes
9. Final Rinse - D.I. Water 160°F 1/2 to 1 minute
10. Dry

The PHOSPHATE-FLUORIDE TREATMENT (STABILIZED) is accomplished in the same manner except that the Acid Pickle (Step 4) is modified as indicated below:

*Standard Acid Pickle
Nitric Acid (70%) - 40.0-50.0 fl oz/gal
Hydrofluoric Acid (70%) - 2.0-3.0 fl oz/gal
Water - Remainder

Modified Acid Pickle
Nitric Acid (70%) - 40.0-50.0 fl oz/gal
Hydrofluoric Acid (70%) - 2.0-3.0 fl oz/gal
Sodium Sulfate - 2.5-3.0 oz/gal
Water - Remainder

SOLUTION CONTROL

Process Control Analysis Procedures

The initial task under this program was to determine standard analysis techniques which would be suitable for routine process control.

Solution Preparation

One gallon of each of the following solutions was prepared:

1. HNO_3 (70%) - 40 fl oz/gal
   HF (70%) - 2 fl oz/gal
   $NaSO_4$ - 2.5 oz/gal
2. HNO_3 (70%) - 50 fl oz/gal
   HF (70%) - 3 fl oz/gal
   $NaSO_4$ - 3 oz/gal
3. HNO_3 (70%) - 40 fl oz/gal
   HF (70%) - 3 fl oz/gal
   $NaSO_4$ - 2.5 oz/gal
4. HNO_3 (70%) - 50 fl oz/gal
   HF (70%) - 2 fl oz/gal
   $NaSO_4$ - 3 oz/gal

Titanium metal was then added to 500 ml portions of each solution in amounts equivalent to 0.01, 0.1, 0.5 and 1.0 oz/gal.

The following materials were used in preparation of the solutions:

Nitric Acid, Reagent Grade, 69-71%, A.C.S.
Hydrofluoric Acid, Technical Grade, 70%, O-H-795
Sodium Sulfate, Decahydrate, Crystal, Reagent Grade, A.C.S.
Titanium Metal, 99%, Powder, 100 mesh
Water, Distilled

The solutions were then analyzed utilizing the following procedures:

Analysis Procedures

Nitric - Hydrofluoric Acids

1. Pipette 5 ml sample into a 250 ml flask containing 10 ml of water and 3-4 drops phenolphthalein indicator.

2. Titrate to a phenolphthalein end point with 0.4 N NaOH. Record as mls "A".

3. To this same solution, add 30 gms C.P. NaCl. Adjust pH to just alkaline (pink) to phenolphthalein using dilute HCl or NaOH.

4. Heat to 70°-80°C (158°-176°F).

5. Add 3-4 drops methyl red indicator solution.

6. Titrate immediately to methyl red end point (yellow to red*) with standard aluminum chloride solution. Record as mls "B". (Standard aluminum chloride solution contains 40.24 g/l $AlCl_3 \cdot 6 H_2O$).

   *End points should be checked against standard solutions. Fresh nitric-HF solutions normally turn yellow when methyl red indicator is added. Used solutions will require adjustment with 0.4N NaOH after methyl red indicator is added.

   Calculations:
   1. B X 0.6 = fl. oz/gal 70% HF
   2. fl oz/gal HF X 4 = ml 0.4 N NaOH required for HF.

3. A - (2 above) = mls 0.4 N NaOH required for Nitric.
4. (3 above) X 0.65 = fl oz/gal 70% HNO_3

This procedure appears to be suitable for control of the acid solution. Technique is important and some practice is required in the identification of the correct end point.

Sulfates in Nitric Hydrofluoric Acid Solutions

1. Pipette a 10 ml sample into a beaker add 100 ml water. Filter into a 400 ml beaker and wash paper thoroughly with water.

2. Heat to near boiling and add 15 ml of 20% barium chloride solution slowly while stirring constantly. Keep at boiling for 15 minutes. Add filter pulp and allow to settle for 15 minutes.

3. Filter through #42 Whatman paper (or equivalent), wash 6 times with dilute hydrochloric acid, barium chloride solution and 6 times with hot water. Check filtrate with barium chloride to determine if precipitation is complete.

4. Transfer precipitate and paper to a dried and weighed crucible. Char the paper, then ignite at 900°C for 1 hour, cool and weigh as barium sulfate.

5. Calculate - g $BaSO_4$ X 8.04 = oz/gal Na_2 SO_4

The initial analysis of the prepared solutions indicated a sulfate content somewhat lower than the calculated amount should produce. This could have been caused by a variation in the water content of the sodium sulfate, decahydrate used to prepare the solutions. Therefore, an additional solution was prepared using anhydrous sodium sulfate and reagent grade acids. This solution, when analyzed, had a sulfate content near that which was calculated. During further study, it was found that the technique used during the gravimetric procedure was faulty and a complete precipitation of the sulfate had not been accomplished. Additional analysis of the original stock solutions produced satisfactory sulfate results. (See Table I.)

It was noted during this study that the technical grade hydrofluoric acid may contain varying amount of sulfate. Federal Specification O-H-795, Hydrofluoric Acid, Technical, requires a minimum of 60% HF by weight, but it does not limit the sulfate content. On the other hand, O-N-350, Nitric Acid,

Technical, allows up to 0.5% by weight calculated as sulfuric acid. Therefore, a sulfate determination on both the hydrofluoric and nitric acids is recommended when extremely close control of sulfates is desired. Analysis of the stock solutions prepared for this evaluation indicated approximately 0.5 oz/gal sulfate in a solution of 50 fl oz/gal nitric acid and 3 fl oz/gal hydrofluoric acid. This appeared to be about one-half from the nitric acid and about one-half from the hydrofluoric acid.

The results reported in Table I appear to be high by about the same amount as the sulfate content of the acids.

In addition to the gravimetric procedure, a general procedure for the indirect determination of sulfates by Atomic Absorption was used. This procedure was taken from the Perkin-Elmer literature dated March 1971. It includes the following steps:

1. Preparation of standard stock solution. Dissolve 1.479 g of anhydrous sodium sulfate in 1 liter of water. This solution will contain 100 μg/ml sulfate. Prepare standards by dilution.

2. Prepare sample by diluting 2.5 ml to 500 ml. (1:200).

3. Pipette 10 ml of sample solution into a 25 ml volumetric flask. Add 1 drop concentrated HCl, 1 ml KCl solution and 10 ml of 200 μg/ml barium chloride solution. Make to volume, let set overnight.

4. Analyze different dilutions of the stock solution and plot a calibration graph.

5. Analyze the excess barium in the sample using standard condition for the Atomic Absorption instrument being used.

The results produced by this method indicate a relationship between the sulfate content and the amount of dissolved metal. This is shown below:

Solution Number and Condition	Sulfate Results (AA)
#1 40 fl oz/gal HNO_3	
2 fl oz/gal HF	
2.5 oz/gal Ha_2SO_4	2.5 oz/gal
Titanium Metal Added	
.01 oz/gal	2.8 oz/gal
.1 oz/gal	3.0 oz/gal
.5 oz/gal	3.15 oz/gal
1.0 oz/gal	4.0 oz/gal

Solution Number and Condition	Sulfate Results (AA)
#2 50 fl oz/gal HNO_3	
3 fl oz/gal HF	
3.0 oz/gal Na_2SO_4	3.1 oz/gal
Titanium Metal Added	
.01 oz/gal	3.6 oz/gal
.1 oz/gal	4.0 oz/gal
.5 oz/gal	4.6 oz/gal
1.0 oz/gal	4.7 oz/gal

These results prompted several modifications of the general procedure.

The first modification involved substituting nitrate salts for the chloride salts and adding boric acid to complex the fluoride ion. The second modification involved the use of hydrogen peroxide as a complexing agent for the titanium ion, and the third modification was directed toward precipitation and removal of the titanium before analysis. None of these methods appeared to affect the sulfate results to any appreciable extent.

It appears that the interference may be caused by something other than titanium. Additional work on used solutions would be needed to provide an acceptable procedure.

There are a number of volumetric procedures for the determination of sulfates. However, in most of these, interference is caused by either nitrates, fluorides or dissolved metals such as aluminum, vanadium, and titanium. The separations necessary make most of these methods unattractive from a standpoint of time required.

One method which appears promising involves titrating a buffered aliquot of the pickle solution with standard (0.025N) barium chloride using THQ (Tetrahydroxyquinone) as an indicator. However, the nitric and hydrofluoric acids interfere and must be removed before repeatable results can be obtained (Reference 5).

Based on these results, it appears that the gravimetric procedure is the most suitable for routine process control at this time.

Titanium Metal in Nitric-Hydrofluoric Acid Solution

The titanium metal content was determined by Atomic Absorption using the following general procedure.

1. Prepare standard - dissolve 1.000g titanium metal with 100 ml 1:1 HCl. Dilute to 1 liter.

2. Make up desired standards by diluting stock solution (above) with 10% (V/V) HCl.

3. Set up A.A. unit (Perkin-Elmer 306)
   Wavelength - 3653 UV
   Slit setting - 3
   Flame (Rich) - Nitrous Oxide - Acetylene
   Linearity: Linear to concentrations of 200 μg/ml

4. Prepare sample. Dilute 20 ml of pickle solution to 2000 ml for 0.01 oz/gal Ti solution. Dilute other samples as necessary.

5. Analyze samples.

Phosphate-Fluoride Treatment Solution

The phosphate-fluoride solution was controlled by maintaining the free acid content. The analysis procedure is as follows:

Free Acid

1. Pipette a 10 ml sample into a 250 ml flask, add about 75 ml water.

2. Add 3-4 drops phenolphthalein indicator.

3. Titrate to a pink end point with 0.4 N NaOH.

Calculation:

mls (0.4N NaOH) X 0.08 = % by wt.

of free acid expressed as HF

The solution is maintained by adding proportional amounts of the constituents used in the initial makeup.

An interesting procedure for this analysis is the use of specific ion electrodes. The total acid is determined by titration and the fluoride ion content determined by specific ion electrode. The nitric acid and hydrofluoric acid concentrations can then be calculated. This method can also be adapted for use in analyzing the phosphate-fluoride solutions. It appears that all constituents of the bath can be accurately determined by this method.

SOLUTION LIFE

The term solution life is defined, for the purpose of this report, as the rate at which a solution depletes with use. It does not take into account airborne contamination, drag over from other processes, and misuse or abuse by the processing of materials other than that intended. The solutions used in this evaluation were covered when not in actual use and were used for processing C.P. titanium only.

The initial check on acid consumption was during the weight loss determination. The surface area of the titanium sheet pickled in each 1000 ml of solution was 2.25 sq. ft. which would be equivalent to about 8 sq. ft/gal.

The analysis of the solutions before and after use indicates essentially no change in acid concentration.

Solution No.	Initial Concentration	After Use
1. HNO_3	40.2 fl oz/gal	39.9 fl oz/gal
HF	2.4 fl oz/gal	2.3 fl oz/gal
2. HNO_3	50.2 fl oz/gal	50.5 fl oz/gal
HF	3.4 fl oz/gal	3.2 fl oz/gal
3. HNO_3	50.6 fl oz/gal	50.5 fl oz/gal
HF	3.3 fl oz/gal	3.3 fl oz/gal
4. HNO_3	40.8 fl oz/gal	40.8 fl oz/gal
HF	2.2 fl oz/gal	2.2 fl oz/gal

These results would tend to indicate a very slight consumption of total acid. This fact is also indicated by the analysis of those solutions which were prepared by dissolving known amounts of titanium metal for analysis procedure work. The total acid was changed very little when 1 oz/gal of titanium metal was dissolved in the solution.

The solutions which were used for bondability and durability studies were analyzed periodically and adjusted as necessary to maintain concentrations.

Three solutions were prepared at the following concentrations:

#1 Modified Pickle - Maximum

HNO_3	- 48.3 fl oz/gal
HF	- 3.5 fl oz/gal
Na_2SO_4	- 3.4 oz/gal

#2 Modified Pickle - Minimum

HNO_3	- 39.0 fl oz/gal
HF	- 2.2 fl oz/gal
Na_2SO_4	- 2.5 oz/gal

#3 Regular Pickle

HNO_3	- 43.2 fl oz/gal
HF	- 2.6 fl oz/gal
Na_2SO_4	- none

The solutions were used to prepare bondability test coupons. Approximately 55 sq. ft. of surface area was immersed in the regular pickle (13 gal) and approximately 80 sq. ft. was processed through each of the modified solutions (17 gal). The solutions were analyzed after one half of the panels had been processed and again after all panels were processed.

#1 Modified Pickle - Maximum

	1/2	All
HNO_3	48.1 fl oz/gal	48.0 fl oz/gal
HF	3.1 fl oz/gal	2.5 fl oz/gal
Na_2SO_4	3.5 * oz/gal	3.5 * oz/gal

#2 Modified Pickle - Minimum

HNO_3	38.8 fl oz/gal	38.0 fl oz/gal
HF	1.9 fl oz/gal	1.7 fl oz/gal
Na_2SO_4	2.3 * oz/gal	2.3 * oz/gal

#3 Regular Pickle

HNO_3	44.0 fl oz/gal	44.2 fl oz/gal
HF	2.5 fl oz/gal	2.2 fl oz/gal

*AA analysis results

Based on the results of this test, it appears that the HF is depleted at a faster rate in the modified pickles.

The acid concentrations were then adjusted to the following prior to processing panels for storage life test.

#1 Modified Pickle - Maximum

HNO_3 - 49.4 fl oz/gal
HF - 3.0 fl oz/gal
Na_2SO_4 - 3.5 ** oz/gal

#2 Modified Pickle - Minimum

HNO_3 - 39.1 fl oz/gal
HF - 2.0 fl oz/gal
Na_2SO_4 - 2.7 ** oz/gal

#3 Regular Pickle

HNO_3 - 44.1 fl oz/gal
HF - 2.6 fl oz/gal

**Gravimetric Procedure Results

The storage life test required processing of about 66 sq. ft. of surface through each solution. After this, the acid concentrations were found to be:

#1 Modified Pickle - Maximum

HNO_3 - 49.3 fl oz/gal
HF - 2.6 fl oz/gal

NOTE: #2 Not used for this test.

#3 Regular Pickle

HNO_3 - 44.8 fl oz/gal
HF - 1.7 fl oz/gal

These results show that the HF is depleted at a fairly rapid rate in each solution. In that the HF reacts with the surface oxides on the sheet, the history and condition of the material will cause a variation in the rate of depletion.

Prior to processing panels for the exposure test, the solutions were adjusted to the following acid concentrations.

#1 Modified Pickle - Maximum

HNO_3 - 50.1 fl oz/gal
HF - 2.70 fl oz/gal

#3 Regular Pickle

HNO_3 - 44.8 fl oz/gal
HF - 2.8 fl oz/gal

The exposure test panels comprised approximately 76 square feet of surface area processed through each solution. The solutions were analyzed for acid concentration.

#1 Modified Pickle - Maximum

HNO_3 - 50.1 fl oz/gal
HF - 2.2 fl oz/gal
Na_2SO_4 - 2.7 * oz/gal

#3 Regular Pickle

HNO_3 - 45.1 fl oz/gal
HF - 1.9 fl oz/gal

*AA Analysis Procedure

Again the HF was depleted at about the same rate with very little change in the nitric content. The sulfate content had apparently been depleted. However, subsequent analysis proved this to be in error.

The solutions were then adjusted to the following concentrations prior to processing panels for durability testing.

#1 Modified Pickle - Maximum

HNO_3 - 49.5 fl oz/gal
HF - 3.4 fl oz/gal
Na_2SO_4 - 5.3 oz/gal

The sulfate content was analyzed by the AA procedure and confirmed by the gravimetric procedure. The panels were processed at this concentration.

#3 Regular Pickle

HNO_3 - 48.9 fl oz/gal
HF - 2.9 fl oz/gal

Based on the results of these tests. it appears that 5 square feet of C.P. titanium surface per gallon of solution will deplete the HF content .5-1.0 oz/gal. The nitric acid content will be relatively unaffected by the same amount of titanium. The sulfate content will also remain relatively stable for this amount of surface.

Effect on Metal Properties

Mechanical Properties

Four sets of titanium samples (1" X 10" X .016") were cut from adjacent areas of the same sheet. The samples were processed through the pickle solutions and then subjected to physical properties determination, grain boundary attack, and preferential etching evaluations. In each case, two samples were maintained in an unetched condition as controls and three samples were immersed for two minutes in pickle solutions as follows:

#1 Standard Pickle - Minimum Concentration

HNO_3 - 40 fl oz/gal
HF - 2 fl oz/gal

#2 Standard Pickle - Maximum Concentration

HNO_3 - 50 fl oz/gal
HF - 3 fl oz/gal

#3 Modified Pickle - Minimum Concentration

HNO_3 - 40 fl oz/gal
HF - 2 fl oz/gal

Na_2SO_4 - 2.5 fl oz/gal

#4 Modified Pickle - Maximum Concentration

HNO_3 - 50 fl oz/gal
HF - 3 fl oz/gal
Na_2SO_4 - 3.0 fl oz/gal

After pickling, the control and test samples were machined into tensile test specimens and the physical properties determined. See Table II for test results. The variation between the unetched control specimens and the specimens etched in the modified pickle appeared to indicate an excessive loss of properties when compared to the coupons etched

in the standard pickle. However, the appearance of the coupons did not indicate excessive etching. Therefore, an additional group of coupons were cut from one end of a 3-foot wide sheet. Two specimens were cut from each edge of the sheet and two were cut from a section near the center. These specimens were not cleaned or pickled prior to testing. The test results are recorded in Table II as "Control Test." Note that the spread between the minimum and maximum values is greater than the change caused by the different pickles. It is concluded that a 2-minute immersion in the pickle solution did not materially affect physical properties of the titanium sheet tested.

Samples of the pickled sheet were examined by the Scanning Electron Microscope (SEM) at 100X, 300X, and 1000X magnification (See Figures 1, 2 and 3). There was little overall difference in the appearance of the surfaces. There was no evidence of intergranular attack and the grain boundary etching appeared to be only slightly more severe in the maximum concentration solutions.

Weight Loss and Hydrogen Content

Six 3" X 3" X .016" specimens for each condition were processed through both the standard and the modified pickles at the high and low concentration limits. These specimens were identified, solvent cleaned, dried, and weighed prior to immersion in the pickle solutions for periods of one-half, one, and two minutes. After thorough rinsing and drying, the specimens were again weighed and loss recorded. The weight loss in grams for each specimen is shown in Table III. The weight loss, calculated to milligrams per square foot, is shown in Figure 4.

The results of these tests reinforce the conclusion that a two-minute immersion in the pickle solution does not materially affect the properties of the titanium sheet.

The samples were analyzed by vacuum extraction using a modified Serfass Gas Analyzer. See Table IV for results of the analysis. Each value shown is an average of three or more samples. The pickled samples all indicate a lower hydrogen content than the control, solvent cleaned only, sample. This is not uncommon and it supports the theory that a higher hydrogen concentration is present in the surface layers, and when this is removed by any means, the average hydrogen content is reduced.

BONDABILITY TESTING

Solution Preparation

Solutions were prepared for use in the treatment of bonding test specimens. Approximately 17 gallons of the modified pickle solution were prepared at both the high and low concentration limits. The standard pickle and the phosphate-fluoride treatment solution were prepared at the mid-range of the concentration limits. Approximately 13 gallons of the pickle and 25 gallons of the treatment solution were prepared.

The pickling and surface treatment was accomplished in plastic tanks, and the precleaning, rinsing and water soak operations were accomplished in stainless steel tanks. The step by step procedures, the materials, and the concentrations are listed in the previous section entitled Titanium Surface Treatment.

Preliminary Bondability Tests

Samples for metal-to-metal floating roller peel, blister detection shear, and drum peel were prepared by the phosphate-fluoride process, utilizing a standard pickle solution and a modified pickle solution at both the minimum and maximum concentration. The metal-to-metal peel panels consisted of a thin member .016 X 6 X 18 inches, and a thick member .050 X 6 X 10 inches. The blister detection shear panel was made from 2 pieces .050 X 6 X 10 inches. The drum peel members were .016 X 3 X 10 inches bonded to .5 inch X 3/16 inch cell core. The drum peels were made with both flat face sheets and rigidized face sheets. The rigidized material is commonly used as work decks in engine areas and the flat sheet is used in areas such as firewall and fuel cell cavities.

The panels were bonded with the four different adhesive systems and tested at ambient conditions, -65°F and 180°F. The curing conditions for each adhesive is listed with the test results. All bonding was accomplished in an autoclave. Test results are shown in Tables V, VI, VII, and VIII.

The results of these tests indicate that there is little, if any, discernible difference in the initial bond strength of titanium surfaces prepared by the standard and the modified processes.

Storage Life Prior to Bonding

Metal-to-metal peel specimens were treated with the standard phosphate-fluoride process and with the modified process. Four panels from each group were primed with adhesive primer

and/or placed into the bonding cycle immediately after treatment (within one hour). The remaining panels were wrapped in kraft paper and stored in the laboratory. The panels were bonded with AF126, N227, EA9605 and FM98 adhesives.

An additional set of four specimens from each group were bonded after storage times of 2, 4, 8, 12, 24, 48, 72, 96, 168 and 240 hours.

Each test panel was cut into five one-inch wide strips for floating roller peel test. Two strips were tested as controls, and the remaining three strips were subjected to immersion in water at 140°F for seven days prior to testing. Test results are shown in Tables IX, X, XI and XII. Tested coupons were visually evaluated for extent of water penetration.

Visual examination revealed very little difference between those panels treated with the modified process and those treated by the regular process. In each case, those coupons which were tested immediately after bonding exhibited a cohesive failure and acceptable strength for the adhesive concerned. Those coupons which were subjected to the water immersion test exhibited various amounts of cohesive versus adhesive failure (see Figure 5). The control coupons shown in the center of Figure 5 are typical of the cohesive failure exhibited by AF126 and N227 tested at room temperature. The other coupons, which were subjected to the hot water soak are typical of the variation in adhesive and cohesive failure found in this test.

The average amount of water penetration appeared to be approximately the same on all sets of coupons, except that the 168 and 240-hour out time coupons bonded with AF126 and N227 exhibited an almost complete adhesive failure after the seven-day hot water soak. This would tend to indicate 100 percent moisture penetration or oxide conversion (see Figures 6 and 7). However, this is not reflected accurately by the peel strengths (see Tables XI and XII). The average peel strengths of those coupons bonded immediately after processing and subjected to the hot water soak are about the same as the 168 and 240-hour out time coupons. However, the extent of adhesive failure is much greater on the longer out time coupons.

Laboratory Qualification Testing

MMM-A-132 Environmental Tests

Metal-to-metal peel specimens and blister detection shear panels were prepared by both the standard and modified process.

These panels were bonded with the four adhesives used for previous testing, AF126, N227, EA9605 and FM98. The test coupons were cut to size and the control coupons tested. Two coupons were used for controls from each peel panel and three coupons were exposed to the various media. The shear panels produced three coupons for control and five for exposure.

MMM-A-132 Seven-Day Tests

Test coupons were immersed in JP-4 turbine fuel, MIL-H-5606 hydraulic fluid and MIL-L-7808 turbine oil for seven days. The coupons were removed from the fluid and tested immediately. The results of these tests are shown in Tables XIII, XIV and XV. Visual examination of these coupons indicated no penetration of the immersion media into the bond joint.

MMM-A-132 Thirty-Day Tests

Metal-to-metal peel test panels and blister detection shear test panels were prepared, bonded and cut to size. Control test coupons were tested immediately after bonding. The remaining coupons were exposed to salt spray, 120°F at 95 percent relative humidity, and immersion in tap water for thirty days. After exposure, the test coupons were tested for peel and lap shear strength. These test coupons were placed in a container of water after exposure to prevent drying prior to testing. All testing was completed within six hours after removal from the exposure media. The results of these tests are shown in Tables XVI, XVII, and XVIII.

The visual examination of the thirty-day exposure coupons revealed a definite trend. Those surfaces processed by the modified treatment had less penetration than those treated by the standard method. This is shown in Figures 8, 9 and 10 for N227, Figures 11, 12 and 13 for AF126, Figure 14 for FM98, and Figure 15 for EA9605.

In these figures, the tested peel specimen is shown. The thick member, with most of the adhesive intact, is toward the bottom and the thin member is toward the top. The areas of adhesive failure versus cohesive failure can be seen on the thin member. The area affected by moisture penetration can be seen readily on the N227 specimens. It appears as a streak of adhesive failure along each edge of the specimens processed by the standard treatment. Note the absence of this type of failure on the specimens treated by the modified process. Figure 8 shows one specimen in the modified treatment group that has an area of adhesive failure. However, this failure did not appear to be the same as those on the standard specimens.

The difference in the degree of moisture penetration is more difficult to see on the panels bonded with AF126. However, the extent of adhesive failure is less on those panels treated by the modified process. Figure 12 shows this very well.

Even though the metal-to-metal peel strengths of FM98 and EA9605 are inherently low, a difference in the moisture penetration can be seen. Figures 14 and 15 show the variation in adhesive versus cohesive failure.

This difference in moisture penetration was not seen in the seven-day hot water soak test used in the storage life evaluation. It appears that time of exposure is a critical factor in that the different temperatures did not produce correspondingly different results. The seven-day hot water soak was accomplished at 140°F, the thirty-day humidity test at 120°F, the thirty-day salt spray at 95°F, and the thirty-day water immersion at ambient (75°F). Based on the results of a visual evaluation, the penetration rates are about the same for the three thirty-day tests.

DURABILITY TESTING

Solution Concentration

The solutions, prepared earlier and used throughout the bond test phase, were analyzed and adjusted to the following concentrations, after which the test panels for durability testing were prepared.

Modified Pickle (Maximum Concentration)

Nitric Acid	- 50.1 fl oz/gal
Hydrofluoric Acid	- 2.7 fl oz/gal
Sulfate	- 5.3
Titanium	- 1230 ppm - analyzed only

Standard Pickle

Nitric Acid	- 44.8 fl oz/gal
Hydrofluoric Acid	- 2.7 fl oz/gal

Hot Water Soak Test

Metal-to-metal peel test panels were prepared by both the standard and modified process. The panels were bonded with AF126, N227, FM98 and EA9605. After bonding, the panels were cut into peel test coupons. Two coupons were tested immediately as controls, and the remaining coupons were immersed in water at 140°F for seven days prior to testing. The results of these tests are shown in Table XIX.

The bond strengths exhibited by AF126 and N227, after the seven-day hot water soak, are much higher than those found after the hot water soak in the storage life determination. This has not been fully explained; however, there was little, if any, visible difference in the extent of water penetration on the panels treated with the standard process when compared with those treated by the modified process. The percentage of cohesive failure was much larger on these panels than on those used in the storage life test. This again points up the fact that the seven-day soak test is not satisfactory for surface or adhesive evaluation.

Hot Wet Cyclic Creep

Test panels were prepared by both the standard and modified process and bonded with AF126 and N227 adhesive systems. The test panels were made from four pieces of titanium .050 X 4 X 19 inches. These sections were laminated together into a flat panel which was then cut into strips .5 inch wide. Each strip was notched and drilled to provide ten lap shear test joints. Two strips were selected for creep test and one strip was used for lap shear test.

Figure 16 shows the specimens installed in the test chamber. The float in the bottom of the photograph maintains a constant water level over the heating elements. The temperature in the chamber is thermostatically controlled and the load is applied to the bonded joints by arms attached to the top of each specimen. Each arm is equipped with a microswitch and timer which provides exact time to failure for each joint. After each joint failure, a bolt is inserted through the predrilled holes, the time of failure recorded, the timer switch reset, and the test continued. The specimens are loaded to 1000 psi for sixty minutes and then unloaded for fifteen minutes. This cycle is repeated continuously and the cabinet is maintained at 120°F and 95±5 percent relative humidity. The lap shear strengths of the control coupons are shown in Table XX. The time to failure and order of failure are shown in Tables XXI, XXII, XXIII and XXIV.

In each case, the time of exposure before the first joint failure is longer for the surfaces treated by the modified process. Also, the time of exposure before the twentieth failure is slightly longer for the modified process. An interesting item is the difference in the time to failure between Set #1 and Set #2. With both adhesives and the standard treatment, Set #1 failed completely before the first joint failed in Set #2. These sets were cut from adjacent areas of the same panel for each adhesive, and there have been no significant differences observed in bondline thickness or other adhesive characteristics. Therefore, it is theorized

that the nonuniformity of moisture penetration is caused by a surface condition which is not present on panels processed by the modified treatment.

The average time to failure for twenty joints indicate that the modified process will provide an improvement in the durability of adhesive joints.

PRODUCTION ACCEPTABILITY TESTING

Solution Preparation

A PVC lined steel tank was installed adjacent to the existing standard phosphate-fluoride production process line. The tank was charged with approximately 350 gallons of modified pickle solution. The solution was analyzed after an overnight stabilizing period. The concentration was as follows:

Nitric Acid	- 40.6 fl oz/gal
Hydrofluoric Acid	- 3.0 fl oz/gal
Sodium Sulfate	- 2.5 oz/gal

The phosphate-fluoride solution was analyzed and found to be at 1.63 percent (vol) of total acid. This is within the established control limits of 1.5 to 1.9 percent (vol) total acid. The hot water soak was operating at 152°F which is within the operating range of 145°F to 155°F.

Bonding Tests

These solutions were then used to prepare several peel test coupons for bonding. These were bonded with N227 adhesive and N2271A primer. Peel results were as follows: (PLI)

High 100 Low 85 Average 92.8

These values compare favorably to an average of 92 PLI obtained from a routine day to day process control panel which was processed through the standard phosphate-fluoride treatment on the same day as the evaluation coupons.

After the peel tests were completed, a set of titanium detail parts for an AH-1 engine deck panel, 209-030-209-123, were processed through the stabilized phosphate-fluoride process. The panel was primed, laid up, and bonded by production personnel.

The 209-030-209-123 bonded panel consists of a rigidized titanium upper skin, a flat titanium doubler approximately one and one-half inches wide around the periphery, and another flat doubler along one edge (see Figure 17). The

remainder of the panel is aluminum honeycomb core and reinforced fiberglass skins (See Figure 18).

Destructive Test of Bonded Panel

The 209-030-209-123 panel was cut into sections and subjected to peel and shear tests in accordance with a standard plan which has been developed for routine first article and periodic quality control tests (see Figure 19).

Test results are shown in Table XXV. All values are acceptable.

TABLE I. RESULTS OF SOLUTION ANALYSIS

Solution Number and Condition	HNO_3 (70%) fl oz/gal (1)	HF (70%) fl oz/gal (1)	Na_2SO_4 oz/gal (2)		Ti oz/gal (3)
No. 1 Calculated	40.0	2.0	2.5		-
Analyzed	40.0	2.0	2.9		-
Ti Added .01	39.5	2.2			0.01
0.1	40.0	1.8			0.08
0.5	37.0	2.0			0.52
1.0	38.5	2.0			1.01
No. 2 Calculated	50.0	3.0	3.0		-
Analyzed	50.0	3.1	*2.42	3.4	-
Ti Added .01	49.0	3.2		3.6	0.01
0.1	49.0	3.1		3.4	0.08
0.5	48.0	3.0		3.7	0.52
1.0	48.0	2.7		3.3	1.03
No. 3 Calculated	40.0	3.0	2.5		-
Analyzed	39.0	3.2	3.3		-
Ti Added .01	37.0	3.2	3.1		0.01
0.1	39.0	3.4	3.1		0.08
0.5	39.0	2.6	3.1		0.54
1.0	37.0	2.5	3.1		1.03
No. 4 Calculated	50.0	2.0	3.0		-
Analyzed	49.0	2.2	*2.07	3.4	-
Ti Added .01	49.0	2.3		3.2	0.01
0.1	49.0	2.1		3.2	0.08
0.5	48.0	2.3		3.2	0.54
1.0	48.0	2.2		3.3	1.00
No. 5 Calculated	50.0	3.0	3.0		
Analyzed	50.2	3.1	3.0		-
Ti Added 1.0	50.1	3.1	3.1		-

(1) Analyzed by Volumetric Method
(2) Analyzed by Gravimetric Method
(3) Analyzed by Atomic Absorption

* Initial Analysis - Low Results

TABLE II. PHYSICAL PROPERTIES

Sample Preparation	TEST RESULTS Yield (PSI)	Ultimate (PSI)	Elongation (%)
Standard Pickle			
Minimum Conc.			
Control (No Etch)	72,250	96,150	17.75
2 Min. Etch	76,700	96,333	18.33
Change	+3,450	+ 183	+ .58
% Change	+4.77%	+0.19%	+3.27%
Maximum Conc.			
Control (No Etch)	78,685	98,600	19.5
2 Min. Etch	76,800	97,933	18.5
Change	-1,485	- 667	- 1.5
% Change	-1.88%	-0.67%	-7.69%
Modified Pickle			
Minimum Conc.			
Control (No Etch)	80,700	99,950	19.5
2 Min. Etch	77,733	96,900	19.0
Change	-2,967	-3,050	- 0.5
% Change	-3.67%	-3.05%	-2.56%
Maximum Conc.			
Control (No Etch)	81,000	100,200	18.25
2 Min. Etch	77,333	97,200	18.33
Change	-3,667	- 3,500	+ .08
% Change	-4.52%	- 3.47%	+ .44%
Control Test*			
I Edge	75,900	96,475	21.0
Center	74,700	95,550	22.0
II Edge	79,550	101,550	22.5
% Change (Min to Max)	-6.35%	-5.86%	-6.6%
MIL-T-9046F Type 1, Comp B	70-95 KSI	80 KSI Min	15 Minimum

* Samples cut from end of one sheet. Values are an average of 2 specimens.

TABLE III. WEIGHT LOSS RESULTS

Solution	Weight Loss in Grams Immersion Time 30 Seconds	1 Minute	2 Minutes
#1			
Standard	.0341,.0298	.0583,.0537	.1355,.1283
Pickle	.0479,.0425	.0637,.0570	.1470,.1427
HNO_3 - 40.7	.0468,.0441	.0574,.0643	.1364,.1276
HF - 2.2	Avg. 0.0444	Avg. 0.0591	Avg. 0.1362
#2			
Modified	.0356,.0344	.0465,.0473	.0979,.0890
Pickle	.0343,.0349	.0452,.0488	.0858,.0866
HNO_3 - 40.2	.0347,.0345	.0489,.0474	.0929,.0944
HF - 2.3	Avg. 0.0347	Avg. 0.0474	Avg. 0.0911
Na_2SO_4 - 2.5			
#3			
Standard	.0308,.0326	.0600,.0545	.0971,.1103
Pickle	.0310,.0313	.0557,.0527	.1067,.0994
HNO_3 - 50.6	.0314,.0343	.0570,.0631	.1082,.1043
HF - 3.3	Avg. 0.0319	Avg. 0.0572	Avg. 0.1043
#4			
Modified			
Pickle	0312,.0315	.0432,.0418	.0976,.0975
HNO_3 - 50.1	.0308,.0320	.0438,.0418	.0960,.1010
HF - 3.4	.0306,.0298	.0433,.0437	.0995,.0989
Na_2SO_4 - 3.0	Avg. 0.0309	Avg. 0.0429	Avg. 0.0986

TABLE IV. RESULTS OF HYDROGEN ANALYSIS

Sample Preparation	Average Hydrogen Content
Control (Solvent Cleaned)	36 ppm
Standard Pickle	
Maximum Concentration 2 Minute Immersion.	20 ppm
Standard Pickle	
Minimum Concentration 2 Minute Immersion	15 ppm
Modified Pickle	
Maximum Concentration 2 Minute Immersion	25 ppm
Modified Pickle	
Minimum Concentration 2 Minute Immersion	16 ppm

TABLE V. BONDABILITY TEST RESULTS

ADHESIVE: N227 Batch 611
PRIME: N2271A Batch 57
CURE: 265°F, 60 mins. 40 psi

TEST & CONDITION	SURFACE TREATMENT: STANDARD PICKLE			MODIFIED PICKLE (Maximum)			MODIFIED PICKLE (Minimum)		
METAL TO METAL PEEL (PLI)	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
	5 Coupons Each Test			10 Coupons Each Test					
AMBIENT	84.7	71.9	78.8	74.5	60.4	69.0	77.9	55.7	71.4
180°F	75	63.5	69.2	77.0	60.0	70.9	78.0	64.5	72.8
-67°F	27.3	24.2	24.8	30.0	18.1	23.8	25.7	15.2	21.5
LAP SHEAR (PSI)									
	8 Coupons Each Test			16 Coupons Each Test					
AMBIENT	6220	4720	5257	5060	4460	4837	5140	4380	4796
180°F	3010	2231	2704	3443	2773	3174	3499	3272	3364
-67°F*	7778	5878	7013	9952	6356	7867	7684	5936	6930
	* 1/4" overlap - other values 1/2" overlap								
DRUM PEEL (PLI) FLAT									
	3 Coupons Each Test								
AMBIENT	18.6	17.6	18.2	17.6	17.0	17.2	17.0	14.5	16.2
180°F	16.2	14.6	15.3	17.6	15.6	16.6	16.1	15.1	15.5
-67°F	9.0	9.0	9.0	11.3	10.2	10.8	9.7	9.2	9.5
RIGIDIZED (PLI)									
	3 Coupons Each Test								
AMBIENT	15	10	12	14.0	13.3	13.5	13.3	11.7	12.5
180°F	11.8	8.5	10.0	10.8	8.3	9.8	8.8	7.8	8.5
-67°F	12.5	8.3	10.2	11	6.3	9.4	9.3	8.8	9.1

TABLE VI. BONDABILITY TEST RESULTS

ADHESIVE: AF126 Lot 157 RD
PRIME: EC3909 Lot 18 JIR
CURE: 265°F, 90 min. 40 psi

TEST & CONDITION	SURFACE TREATMENT: STANDARD PICKLE			MODIFIED PICKLE (Maximum)			MODIFIED PICKLE (Minimum)		
METAL TO METAL PEEL (PLI)	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
	5 Coupons Each Test			10 Coupons Each Test					
AMBIENT	75.0	71.8	73.2	70.8	53.8	61.8	85.2	64.7	72.1
180°F	51	45	46.2	52.5	40.5	44.4	54.0	46.5	50.8
-67°F	48.4	30.3	34.5	45.5	24.1	36.0	42.6	21.1	30.1
LAP SHEAR (PSI)									
	8 Coupons Each Test			16 Coupons Each Test					
AMBIENT	4820	4400	4632	4880	4400	4652	5100	4300	4605
180°F	3485	2789	3179	3508	3135	3336	3192	2536	2923
-67°F*	8874	5361	7963	9751	7467	8635	8589	7044	7925
	* 1/4" overlap - other values 1/2" overlap								
DRUM PEEL (PLI) FLAT									
	3 Coupons Each Test								
AMBIENT	28.7	28.7	28.7	29.5	28.6	29.2	31.2	29.5	30.3
180°F	20.3	18.8	19.6	17.7	16.7	17.2	18.7	16.9	18.1
-67°F	20.1	19.6	19.7	15.6	13.6	14.4	17.8	12.8	16.1
RIGIDIZED (PLI)									
	3 Coupons Each Test								
AMBIENT	18.3	16.7	17.2	16.7	15.0	15.8	15.8	12.5	13.6
180°F	9.8	9.2	9.6	10.8	9.3	10.0	10.3	8.0	9.4
-67°F	11.0	10.7	10.9	13.3	12.3	12.8	11.8	9.8	10.8

TABLE VII. BONDABILITY TEST RESULTS

ADHESIVE: EA9605 Lot 076 Roll E
PRIME: None
CURE: 310°F, 90 min, 40 psi

TEST & CONDITION	SURFACE TREATMENT: STANDARD PICKLE			MODIFIED PICKLE (Maximum)			MODIFIED PICKLE (Minimum)		
METAL TO METAL PEEL (PLI)	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
	5 Coupons Each Test			10 Coupons Each Test					
AMBIENT	8	8	8	10	6	7.7	9	6	7.2
180°F	18	14	15.4	21.0	11.9	16.1	19.5	15	18.2
-67°F	3	1.5	2.1	1.5	1.4	1.5	3	1.4	1.6
LAP SHEAR (PSI)									
	8 Coupons Each Test			16 Coupons Each Test					
AMBIENT	3025	2572	2893	3041	2393	2671	2992	2465	2681
180°F	4287	3714	3962	4421	3688	4035	4532	2777	3932
-67°F*	5024	2642	4372	4632	1342	3818	4199	1515	2805
	* 1/4" overlap - other values 1/2" overlap								
DRUM PEEL (PLI) FLAT									
	3 Coupons Each Test								
AMBIENT	16.2	14.5	15.1	15.3	14.5	14.8	12.8	12.0	12.6
180°F	10.1	9.6	9.8	12.2	9.7	11.3	9.7	7.2	8.5
-67°F	6.5	5.5	6.1	5.1	4.1	4.6	6.6	6.1	6.4
RIGIDIZED (PLI)									
	3 Coupons Each Test								
AMBIENT	16.7	16.7	16.7	16.7	13.3	15.6	17.5	13.3	15.5
180°F	7.1	5.7	6.3	12.2	9.0	11.1	10.3	9.5	9.9
-67°F	10.1	8.2	9.2	9.8	8.3	9.1	7.8	6.0	6.7

TABLE VIII. BONDABILITY TEST RESULTS

ADHESIVE: FM98 Batch 1259 Roll 2359
PRIME: None
CURE: 310°F, 90 min, 40 psi

TEST & CONDITION	SURFACE TREATMENT: STANDARD PICKLE			MODIFIED PICKLE (Maximum)			MODIFIED PICKLE (Minimum)		
METAL TO METAL PEEL (PLI)	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
	5 Coupons Each Test			10 Coupons Each Test					
AMBIENT	4	3	3.6	5	3	3.2	4	2	2.3
180°F	6	3	3.6	3	2	2.3	3	2	2.7
-67°F	3	1.5	2.3	3	1.4	1.6	1.5	1.4	1.5
LAP SHEAR (PSI)									
	8 Coupons Each Test			16 Coupons Each Test					
AMBIENT	2716	1532	2273	2634	1856	2232	2691	1694	2243
180°F	4306	3316	3754	3659	2195	2936	3876	2441	3208
-67°F*	5882	1375	3143	4640	1696	2787	4766	1430	2799
	* 1/4" overlap - other values 1/2" overlap								
DRUM PEEL (PLI) FLAT									
	3 Coupons Each Test								
AMBIENT	19.3	15.2	17.6	18.7	17.0	17.6	18.7	18.7	18.7
180°F	20.2	16.2	18.0	13.3	8.0	11.0	19.2	14.8	17.1
-67°F	10.1	8.6	9.2	11.7	7.7	9.5	8.6	6.6	7.2
RIGIDIZED (PLI)									
	3 Coupons Each Test								
AMBIENT	16.7	16.7	16.7	15	10	12.6	16.7	13.3	15.3
180°F	16.3	15.9	15.7	11.8	8.3	10.4	14.2	12.0	13.2
-67°F	13.8	10.8	12.8	12.3	10.8	11.3	16.3	10.8	13.5

TABLE IX

FM98

STORAGE LIFE TEST RESULTS

FLOATING ROLLER PEEL (PLI)

	STANDARD PICKLE						MODIFIED PICKLE					
	CONTROL			WATER SOAK			CONTROL			WATER SOAK		
Hrs	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg
IMM	5	3	4	2	1	1.3	3	2	2.5	2	1	1.3
2	4	3	3.5	2	1	1.3	3	3	3.0	3	1	1.7
4	4	2	3.0	2	1	1.3	3	2	2.5	1	1	1
8	4	3	3.5	2	1	1.3	3	2	2.5	2	1	1.3
12	5	3	4.0	1	1	1	2	2	2.0	2	1	1.3
24	3	2	2.5	2	1	1.7	3	2	2.5	2	2	2.0
48	2	2	2.0	2	2	2.0	2	2	2.0	2	2	2.0
72	2	2	2.0	2	1	1.3	2	2	2.0	2	1	1.7
96	2	1	1.5	2	1	1.3	3	2	2.5	2	1	1.7
168	4	2	3.0	2	1	1.3	4	3	3.5	2	1	1.3
240	3	3	3.0	2	1	1.3	3	2	2.5	2	1	1.7

TABLE X

EA9605

STORAGE LIFE TEST RESULTS

FLOATING ROLLER PEEL (PLI)

	STANDARD PICKLE						MODIFIED PICKLE					
	CONTROL			WATER SOAK			CONTROL			WATER SOAK		
Hrs	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg
IMM	10	8	9.0	4	2	3.0	9	8	8.5	6	2	3.3
2	10	8	9.0	5	3	3.7	13	8	10.5	8	2	4.0
4	8	8	8.0	3	2	2.7	8	7	7.5	3	2	2.7
8	7	6	6.5	2	2	2.0	7	6	6.5	3	2	2.7
12	8	8	8.0	3	2	2.3	8	7	7.5	3	2	2.7
24	8	7	7.5	8	6	6.7	10	8	9.0	9	6	7.0
48	8	7	7.5	9	6	7.3	10	10	10.0	8	7	7.7
72	8	7	7.5	3	2	2.7	9	8	8.5	3	2	2.7
96	8	8	8.0	6	3	4.0	12	9	10.5	3	2	2.3
168	7	6	6.5	3	3	3.0	7	7	7.0	3	2	2.3
240	10	8	9.0	9	4	6.0	9	9	9.0	10	3	5.7

TABLE XI

N227

STORAGE LIFE TEST RESULTS

FLOATING ROLLER PEEL (PLI)

STANDARD PICKLE							MODIFIED PICKLE					
CONTROL				WATER SOAK			CONTROL			WATER SOAK		
Hrs	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg
IMM	70	70	70	32	16	22.0	74	70	72	46	12	24.7
2	74	72	73	34	22	26.7	84	80	82	62	48	56.7
4	72	70	71	42	22	31.3	72	70	71	52	30	38.7
8	70	68	69	34	20	24.7	74	68	71	48	20	32.7
12	72	70	71	38	28	32.0	76	74	75	44	24	30.7
24	74	74	74	58	58	58	84	76	80	60	40	51.3
48	80	74	77	22	14	18	86	80	83	64	18	34.7
72	72	70	71	44	30	36	74	72	73	62	56	60
96	84	76	80	40	20	27.3	84	80	82	62	24	44.7
168	90	80	85	14	10	12.7	88	84	86	48	12	24.7
240	92	86	88	20	14	17.3	88	86	87	30	28	28.7

TABLE XII

AF126

STORAGE LIFE TEST RESULTS

FLOATING ROLLER PEEL (PLI)

STANDARD PICKLE							MODIFIED PICKLE					
CONTROL				WATER SOAK			CONTROL			WATER SOAK		
Hrs	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg	Hi	Low	Avg
IMM	80	72	76	50	16	30	82	80	81	26	22	23.3
2	74	70	72	60	44	50	76	74	75	56	22	36
4	76	70	73	54	20	32	66	62	64	20	10	15.3
8	84	80	82	38	22	27.3	74	72	73	54	34	40.7
12	80	70	75	44	24	30.7	80	70	75	30	18	22
24	80	76	78	50	44	46	80	74	77	30	24	26.7
48	80	70	75	62	40	47.3	60	60	60	28	18	23.3
72	60	56	58	30	18	23.3	70	70	70	28	18	23.3
96	64	60	62	30	10	18	80	76	78	30	18	24
168	70	65	67	54	24	36.6	75	50	62	38	6	18.7
240	80	75	77	60	16	37.3	75	70	72	24	7	14.3

TABLE XIII

JP-4 FUEL IMMERSION TEST

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
AF126						
Peel						
Control	80	76	78	80	78	79
Exposed	60	57	59	84	78	80
Shear						
Control	5141	4757	4914	4981	4563	4766
Exposed	5172	4294	4784	4797	4235	4626
N227						
Peel						
Control	75	73	74	75	74	74.5
Exposed	72	68	70	84	80	82
Shear						
Control	5198	4950	5082	5447	5020	5218
Exposed	5542	5231	5346	5327	4940	5183
EA9605						
Peel						
Control	10	9	9.5	11	10	10.5
Exposed	10	10	10	12	11	11.7
Shear						
Control	3800	3674	3726	3450	3168	3331
Exposed	4075	3574	3838	4124	3760	3962
FM98						
Peel						
Control	3	2	2.5	2	2	2
Exposed	1	1	1	3	2	2.3
Shear						
Control	2386	2197	2274	2649	2386	2478
Exposed	2687	2023	2310	2768	2485	2624

TABLE XIV

7808 OIL IMMERSION TEST

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
AF126						
Peel						
Control	49	36	42.5	84	82	83
Exposed	55	33	42.5	80	78	79
Shear						
Control	4917	4905	4911	4749	4579	4655
Exposed	5173	4729	4937	5263	4738	4921
N227						
Peel						
Control	84	75	80	84	80	82
Exposed	80	75	77.6	82	75	77.3
Shear						
Control	4961	4767	4864	5161	4990	5067
Exposed	5543	4946	5214	5544	5125	5387
EA9605						
Peel						
Control	10	9	9.5	11	9	10
Exposed	10	10	10	10	10	10
Shear						
Control	4022	3541	3770	3625	3377	3536
Exposed	4223	3873	3975	4235	3700	3975
FM98						
Peel						
Control	2	2	2	2	2	2
Exposed	2	2	2	2	2	2
Shear						
Control	2772	2397	2586	2135	1452	1778
Exposed	2947	2148	2546	2439	2024	2196

TABLE XV

5606 FLUID IMMERSION TEST

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	low	Avg
AF126						
Peel						
Control	54	50	52	67	60	63.5
Exposed	64	54	60	78	72	76
Shear						
Control	4981	4734	4850	4942	4029	4454
Exposed	5146	4671	4906	5146	4393	4826
N227						
Peel						
Control	80	80	80	82	80	81
Exposed	79	70	73.6	86	74	80
Shear						
Control	5261	5178	5226	5212	4688	4864
Exposed	5536	5020	5248	5371	4850	5103
EA9605						
Peel						
Control	10	9	9.5	12	11	11.5
Exposed	9	8	8.3	12	12	12
Shear						
Control	4159	3690	3922	4008	3629	3828
Exposed	4151	3669	3945	4490	3669	4041
FM98						
Peel						
Control	2	2	2	3	2	2.5
Exposed	3	2	2.3	3	2	2.3
Shear						
Control	2344	1996	2148	2528	2288	2415
Exposed	2617	1840	2222	2735	2214	2491

TABLE XVI

30-DAY SALT SPRAY TEST

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
AF126						
Peel						
Control	55	55	55	85	80	82.5
Exposed	12	5	9	25	20	21.3
Shear						
Control	4949	4687	4794	5039	4453	4736
Exposed	4734	3958	4314	4462	3614	3987
N227						
Peel						
Control	85	75	80	72	70	71
Exposed	70	55	65	75	50	65
Shear						
Control	5151	4887	5042	5429	5040	5248
Exposed	5219	4802	4986	5142	3948	4540
EA9605						
Peel						
Control	5	3	4	8	6	7
Exposed	1.5	1.5	1.5	7	5	6
Shear						
Control	3822	3587	3726	4097	3745	3867
Exposed	4412	3321	3883	4880	3333	4073
FM98						
Peel						
Control	1	1	1	6	2	4
Exposed	1	0	6	2.4	2	2.1
Shear						
Control	2885	2139	2418	2656	2160	2460
Exposed	2854	1624	2106	2106	1622	1889

TABLE XVII

30-DAY 95% RELATIVE HUMIDITY TEST

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
AF126						
Peel						
Control	75	70	72.5	85	83	84
Exposed	40	40	40	45	12.5	24.8
Shear						
Control	5042	4736	4861	4655	4339	4456
Exposed	4675	3913	4276	4562	3929	4199
N227						
Peel						
Control	80	75	77.5	80	75	77.5
Exposed	65	50	58.3	75	75	75
Shear						
Control	5270	4766	5073	5102	4847	5066
Exposed	4638	3266	3997	5048	4358	4738
EA9605						
Peel						
Control	10	6	8.5	7	7	7
Exposed	12	2.5	5.8	10	5	7
Shear						
Control	3782	3617	3721	4728	3552	4111
Exposed	3518	2535	2986	3275	3053	3178
FM98						
Peel						
Control	2	2	2	4	4	4
Exposed	1	0	0.6	2	1.5	1.8
Shear						
Control	2114	1992	2051	2072	1883	1966
Exposed	2676	1327	1808	1642	1290	1482

TABLE XVIII

30-DAY WATER IMMERSION

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
AF126						
Peel						
Control	75	70	72.5	90	85	87.5
Exposed	70	20	43.3	80	70	76.6
Shear						
Control	5029	4912	4968	4717	4327	4470
Exposed	5019	4406	4790	4956	4442	4742
N227						
Peel						
Control	80	75	77.5	87	80	83.5
Exposed	75	65	71.6	80	70	76.6
Shear						
Control	5194	5070	5132	5049	4411	4757
Exposed	5291	4934	5118	5157	4990	5080
EA9605						
Peel						
Control	10	7	8.5	11	10	10.5
Exposed	12	3	5.8	6	6	6
Shear						
Control	4092	3855	3975	4372	3889	4058
Exposed	4640	4165	4515	4809	2840	4087
FM98						
Peel						
Control	1	1	1	3	2	2.5
Exposed	1	0.5	0.8	2	1	1.5
Shear						
Control	4032	2350	2977	*1360	*1188	*1302
Exposed	3246	2392	2954	2921	2355	2685

*Unable to account for these low values.

TABLE XIX
PEEL TEST RESULTS (PLI)
HOT WATER SOAK TEST
(2 PANELS WITH EACH ADHESIVE SYSTEM)

Adhesive & Condition	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
AF126 (a)						
Control	45	40	42.5*	70	62	66
Exposed	6.0	4.5	5.0*	70	60	63
AF126 (b)						
Control	80	80	80	70	65	67
Exposed	70	60	65	60	50	53
N227 (a)						
Control	70	70	70	85	65	75
Exposed	68	55	62	80	60	68
N227 (b)						
Control	70	65	67	75	70	72
Exposed	80	75	75	70	65	68
FM98 (a)						
Control	8	5	6.5	2	1	1.5
Exposed	3	0.5	1.6	3	2	2.5
FM98 (b)						
Control	3	3	3	2	2	2
Exposed	5	2	3	8	1	3.6
EA9605 (a)						
Control	12	12	12	15	13	14
Exposed	9	7.5	8.3	13	10	11.6
EA9605 (b)						
Control	11	5	8	12	8	10
Exposed	10	5	7.1	15	8	11

(a) Panel No. 1
(b) Panel No. 2

*No reason has been found for these low values.

TABLE XX

LAP SHEAR TEST RESULTS

CONTROL COUPONS FOR THE
WET CYCLIC CREEP TEST

Adhesive System	STANDARD PROCESS High	Low	Avg	MODIFIED PROCESS High	Low	Avg
N227	5257	5115	5184	4971	4689	4829
AF126	5434	4199	4930	5422	5000	5203

TABLE XXI. RESULTS OF HOT WET CREEP TEST

JOINT NUMBER	ORDER OF FAILURE SET #1	ORDER OF FAILURE SET #2	TIME TO FAILURE (HOURS) SET #1	TIME TO FAILURE (HOURS) SET #2
1	(5)	(4)	183.6	520.7
2	(7)	(9)	220.0	861.2
3	(6)	(10)	196.1	865.4
4	(3)	(8)	140.2	839.9
5	(4)	(7)	141.5	545.7
6	(2)	(1)	79.1	507.3
7	(1)	(3)	36.9	520.3
8	(8)	(6)	364.0	525.1
9	(10)	(2)	364.5	508.3
10	(9)	(5)	364.2	521.7

SURFACE PREPARATION PROCESS: STANDARD PHOS-FLUORIDE

ADHESIVE SYSTEM: AF126 - EC3909

FIRST FAILURE: 36.9 TWENTIETH FAILURE: 865.4

AVERAGE TIME TO FAILURE: 415.3

TABLE XXII. RESULTS OF HOT WET CREEP TEST

JOINT NUMBER	ORDER OF FAILURE SET #1	ORDER OF FAILURE SET #2	TIME TO FAILURE (HOURS) SET #1	TIME TO FAILURE (HOURS) SET #2
1	(1)	(6)	384.5	872.5
2	(2)	(7)	453.9	874.8
3	(6)	(8)	465.3	880.3
4	(4)	(1)	460.3	505.3
5	(7)	(9)	698.4	884.1
6	(8)	(5)	707.5	869.8
7	(3)	(4)	460.2	856.4
8	(5)	(2)	461.7	540.4
9	(9)	(9)	732.6	799.6
10	(10)	(10)	759.8	956.8

SURFACE PREPARATION PROCESS: MODIFIED PHOS-FLUORIDE

ADHESIVE SYSTEM: AF126 - EC3909

FIRST FAILURE: 384.5 TWENTIETH FAILURE: 956.8

AVERAGE TIME TO FAILURE: 681.2

TABLE XXIII. RESULTS OF HOT WET CREEP TEST

JOINT NUMBER	ORDER OF FAILURE SET #1	ORDER OF FAILURE SET #2	TIME TO FAILURE (HOURS) SET #1	TIME TO FAILURE (HOURS) SET #2
1	(9)	(2)	243.4	320.7
2	(6)	(3)	233.0	322.2
3	(10)	(1)	244.2	318.1
4	(1)	(10)	193.9	375.6
5	(4)	(7)	206.8	361.6
6	(3)	(6)	197.1	354.5
7	(8)	(8)	241.9	366.1
8	(5)	(9)	221.3	373.9
9	(7)	(4)	236.9	326.4
10	(2)	(5)	197.0	338.9

SURFACE PREPARATION PROCESS: STANDARD PHOS-FLUORIDE

ADHESIVE SYSTEM: N227 - N2271A

FIRST FAILURE: 193.9 TWENTIETH FAILURE: 375.6

AVERAGE TIME TO FAILURE: 283.7

TABLE XXIV. RESULTS OF HOT WET CREEP TEST

JOINT NUMBER	ORDER OF FAILURE SET #1	ORDER OF FAILURE SET #2	TIME TO FAILURE (HOURS) SET #1	TIME TO FAILURE (HOURS) SET #2
1	(2)	(2)	320.4	301.9
2	(1)	(3)	286.5	313.4
3	(3)	(1)	325.4	280.0
4	(4)	(8)	332.4	346.9
5	(8)	(10)	373.2	358.5
6	(6)	(4)	354.9	317.4
7	(7)	(6)	366.7	344.2
8	(10)	(7)	376.9	345.2
9	(5)	(5)	347.4	317.4
10	(9)	(9)	375.4	356.7

SURFACE PREPARATION PROCESS: MODIFIED PHOS-FLUORIDE

ADHESIVE SYSTEM: M227 - N2271A

FIRST FAILURE: 280.0 TWENTIETH FAILURE: 376.9

AVERAGE TIME TO FAILURE: 337.0

TABLE XV. RESULTS OF DESTRUCTIVE TEST

DRUM PEELS	LOCATION	STRENGTH (PLI)
#1	Reinforced Glass Skin	18.3
#2	Titanium Skin	38.3

Lap Shears	Strength (Psi)	Type of Failure
#1 - Ti - Ti	5468	Cohesive Failure
#2 - Ti - Glass	3824	Cohesive Failure
#3 - Ti - Ti	3853	Cohesive Failure
#4 - Ti - Ti	4568	Cohesive Failure
#5 - Ti - Glass	3753	Cohesive Failure
#6 - Ti - Glass	3952	Glass Failure
#7 - Ti - Glass	4059	Cohesive Failure
#8 - Ti - Ti	4420	Cohesive Failure
#9 - Ti - Glass	3197	Glass Failure

Standard Pickle - Minimum Concentration

Standard Pickle - Maximum Concentration

Modified Pickle - Minimum Concentration

Modified Pickle - Maximum Concentration

Figure 1 - 100X Magnification

Standard Pickle - Minimum Concentration

Standard Pickle - Maximum Concentration

Modified Pickle - Minimum Concentration

Modified Pickle - Maximum Concentration

Figure 2 - 300X Magnification

Standard Pickle - Minimum Concentration

Standard Pickle - Maximum Concentration

Modified Pickle - Minimum Concentration

Modified Pickle - Maximum Concentration

Figure 3 - 1000X Magnification

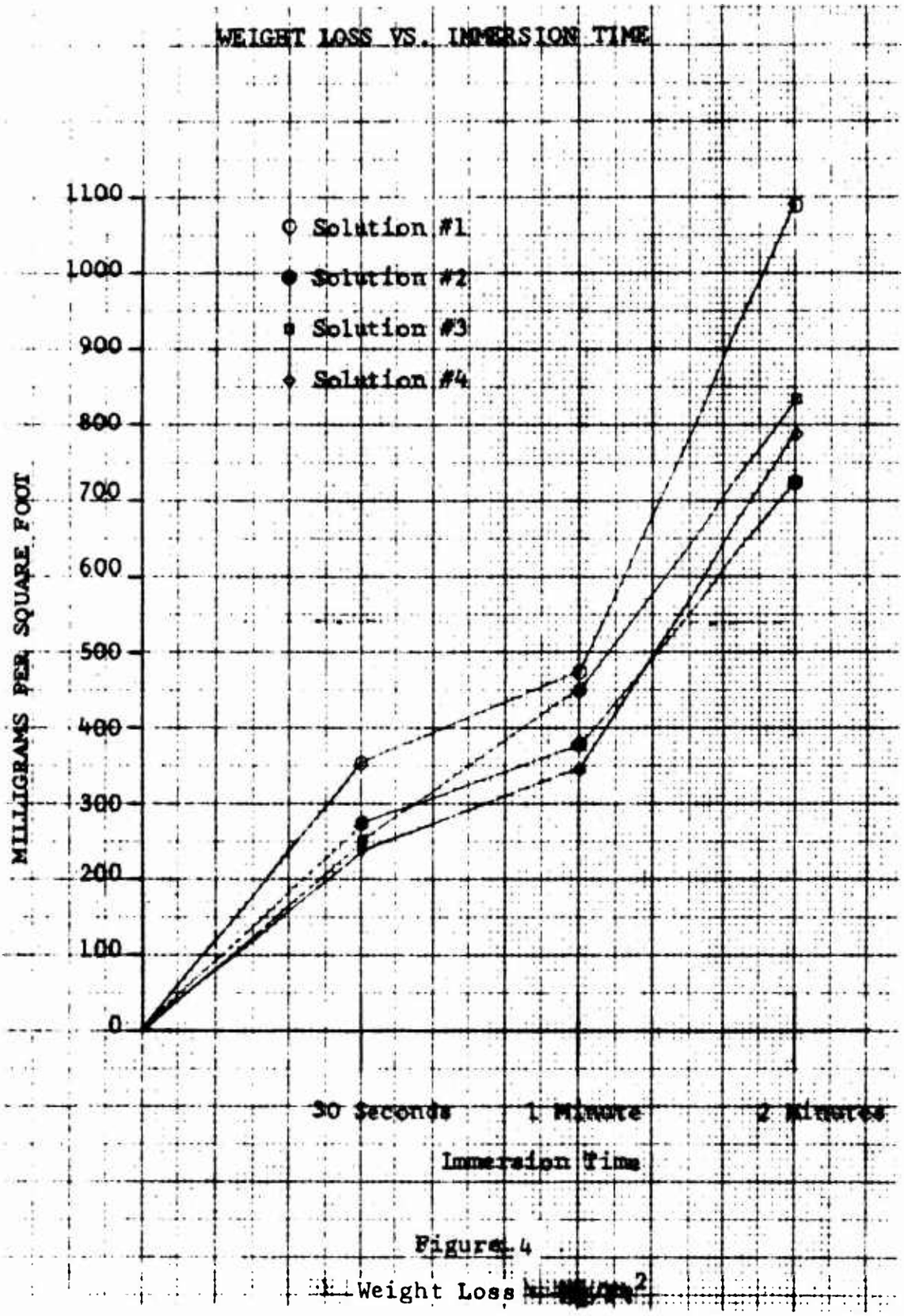

Figure 4

1. Weight Loss

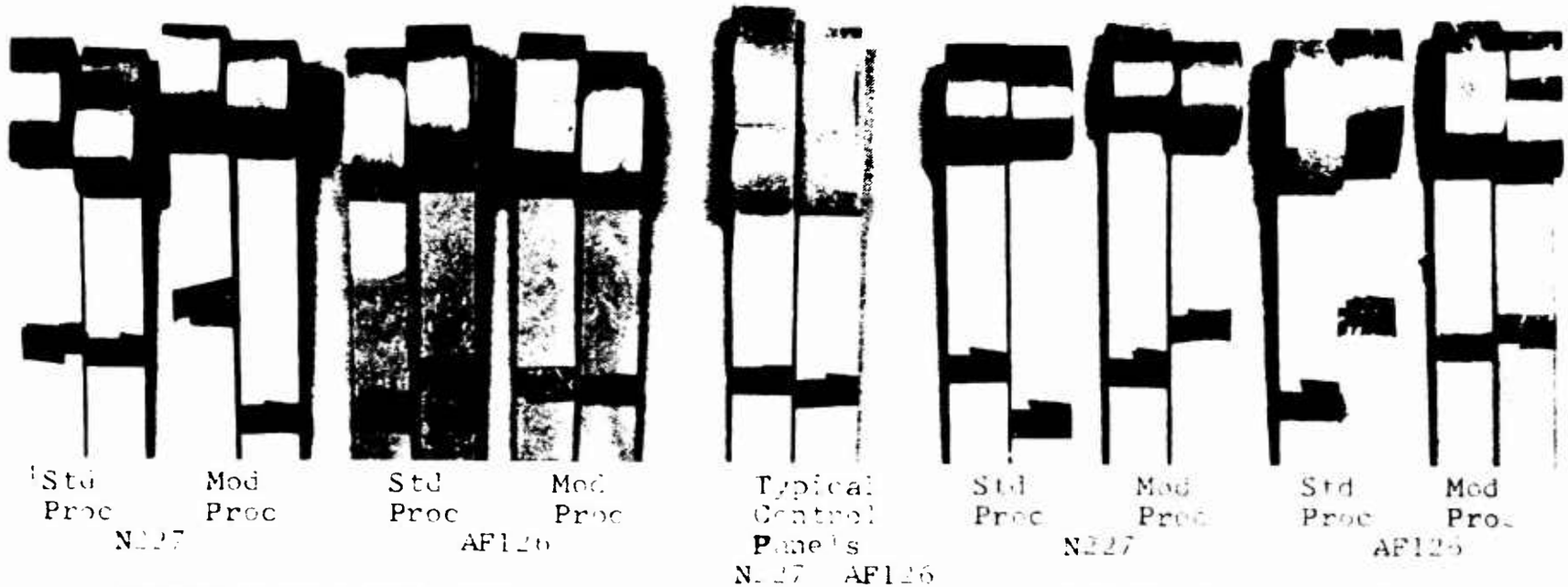

Figure 5 - Adhesive Vs. Cohesive Failure on Peel Test Coupons.

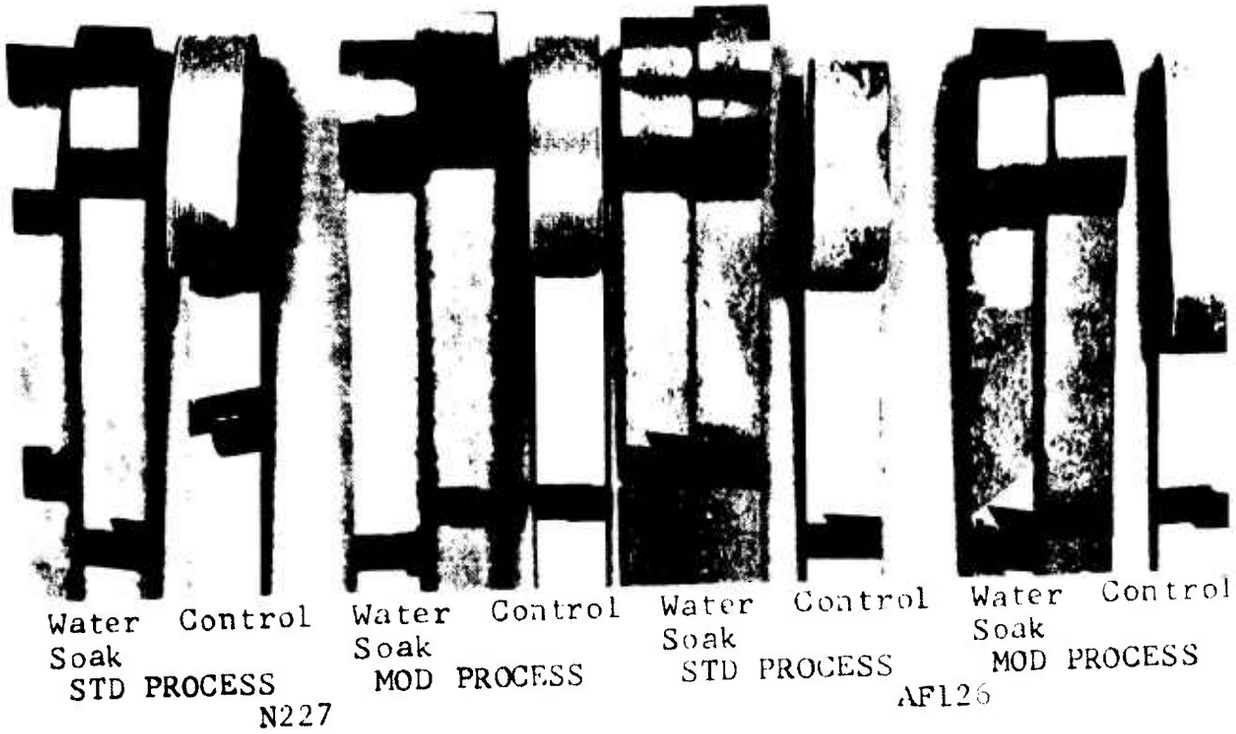

Figure 6 - 168-Hour Storage Life Specimens

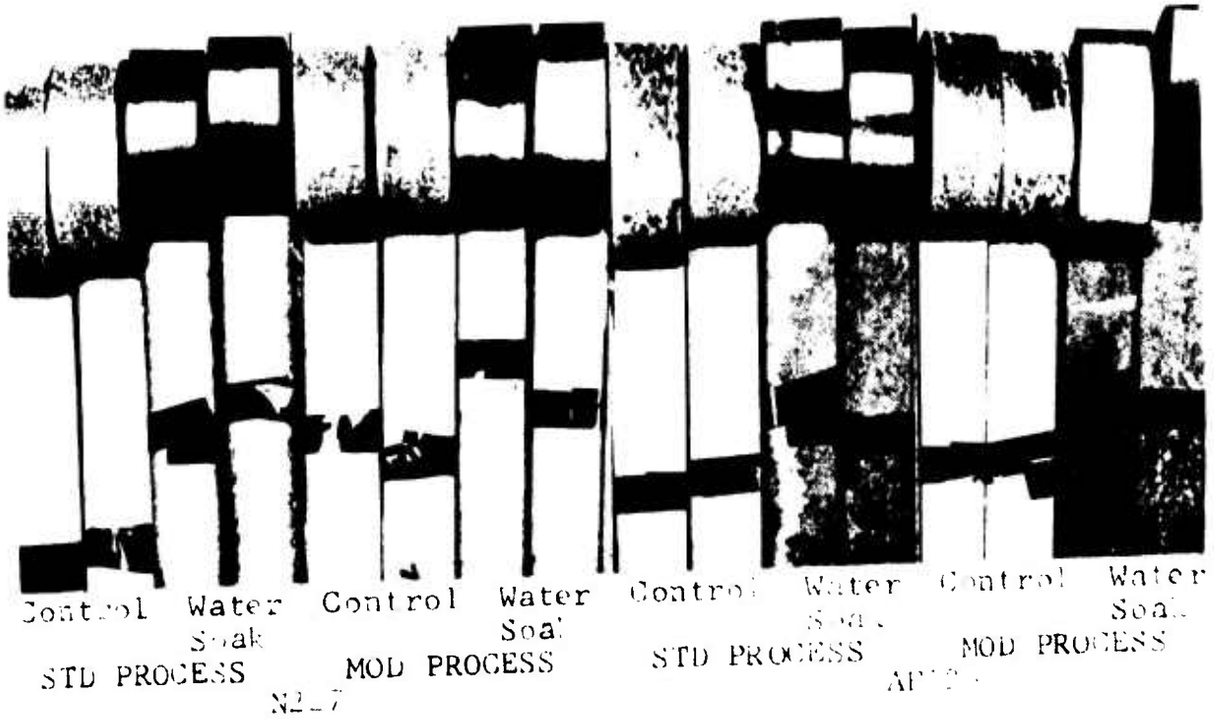

Figure 7 - 240-Hour Storage Life Specimens

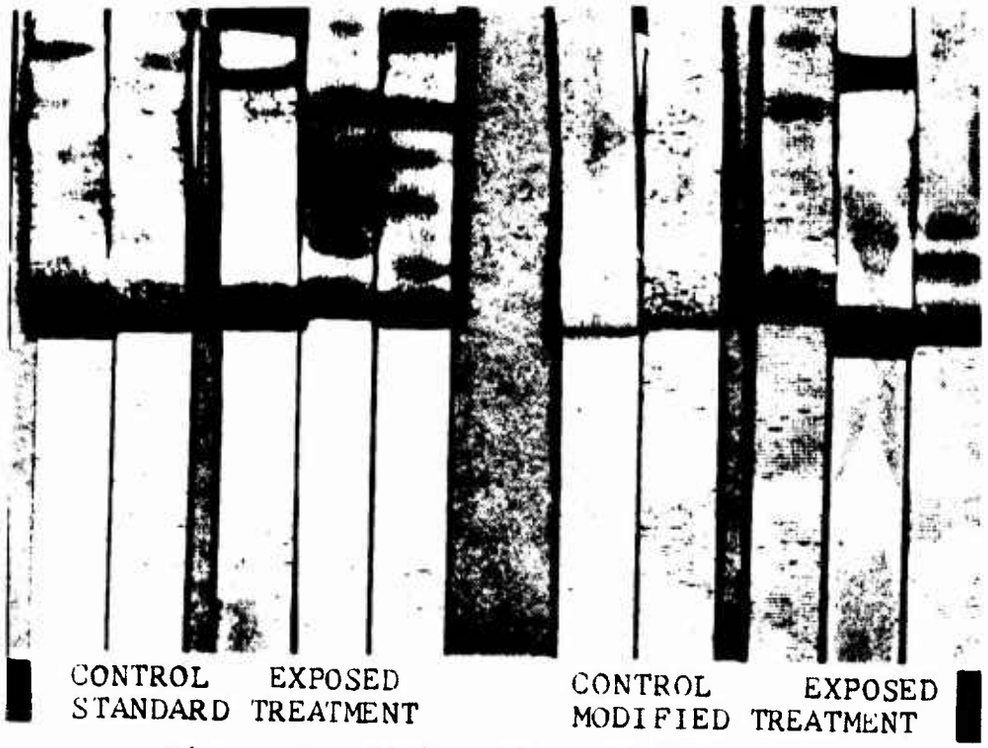

Figure 8 - N227 - After 30-Day
Salt Spray

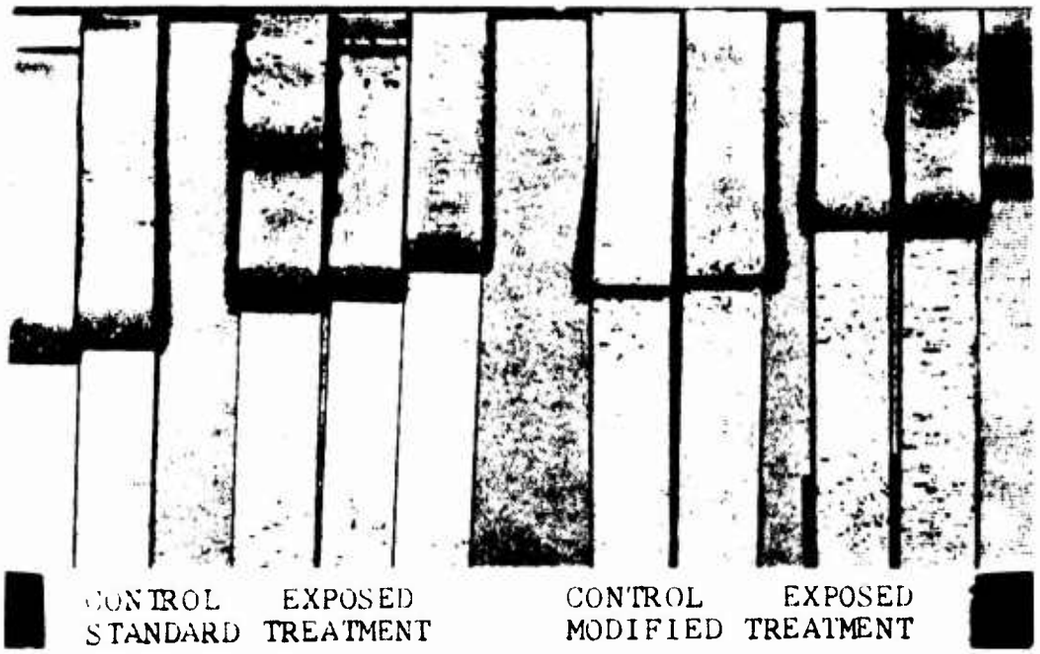

Figure 9 - N227 After 30-Day
Water Immersion

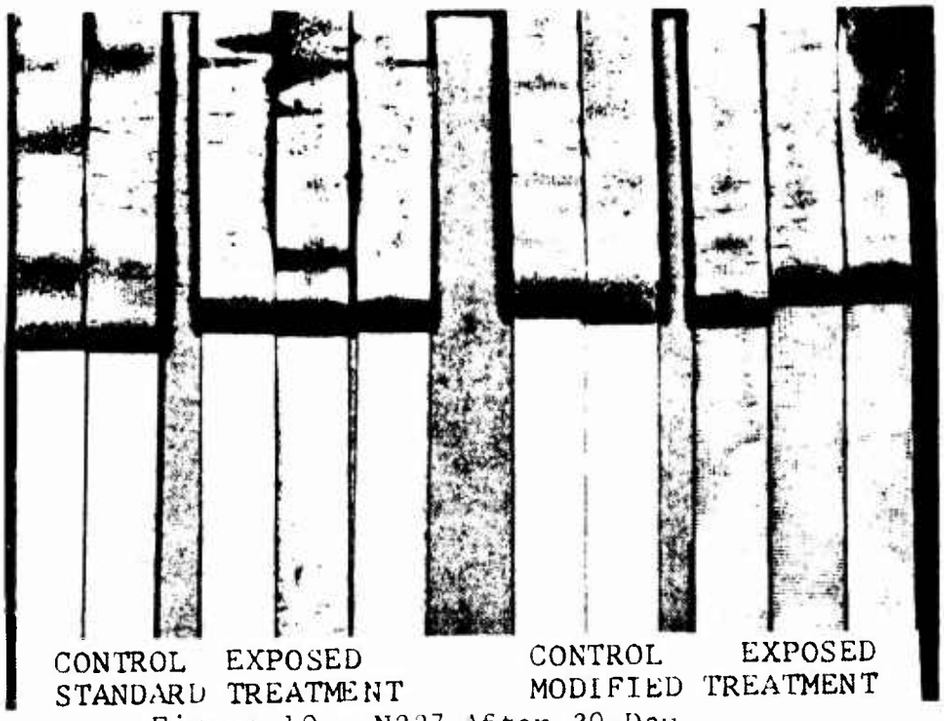

Figure 10 - N227 After 30-Day
95% R.H. - 120°F

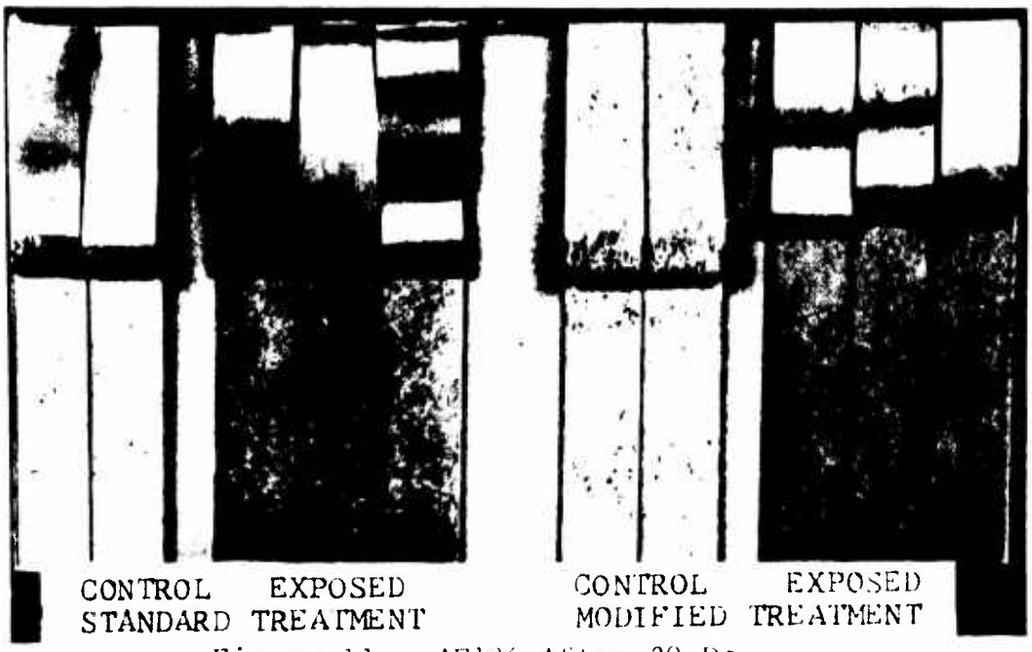

Figure 11 - AF126 After 30-Day
Salt Spray

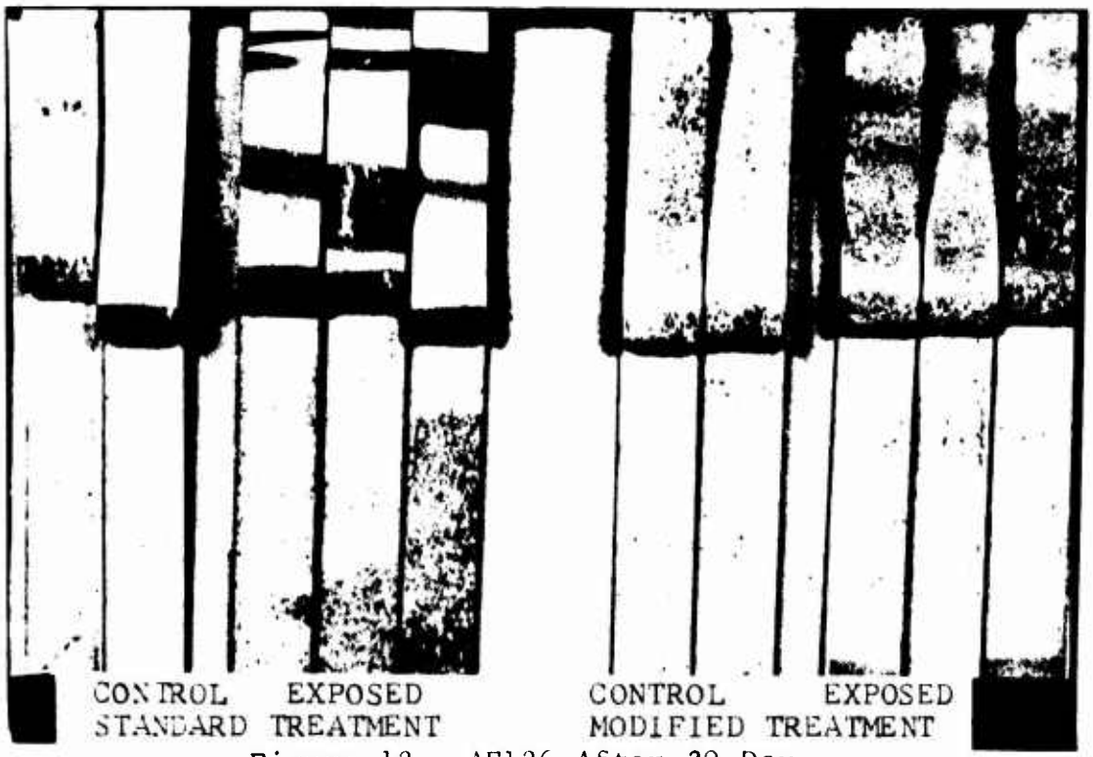

Figure 12 - AF126 After 30-Day Water Immersion

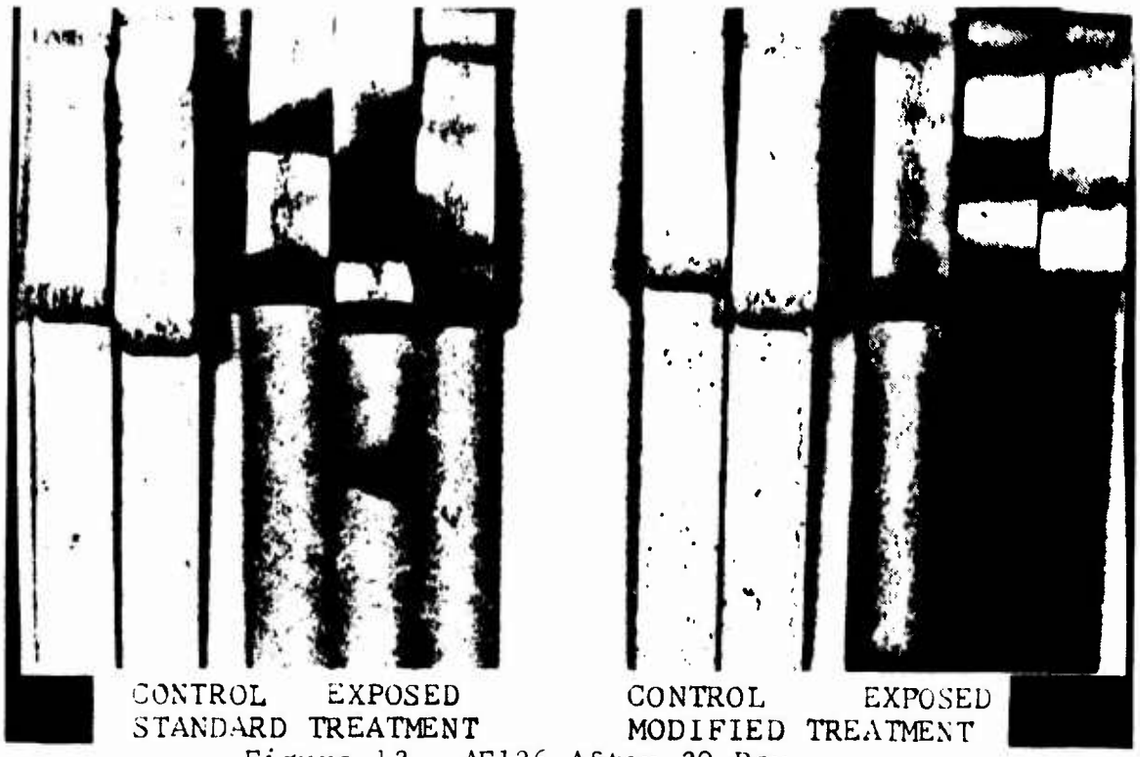

Figure 13 - AF126 After 30-Day 95% R.H. - 120°F

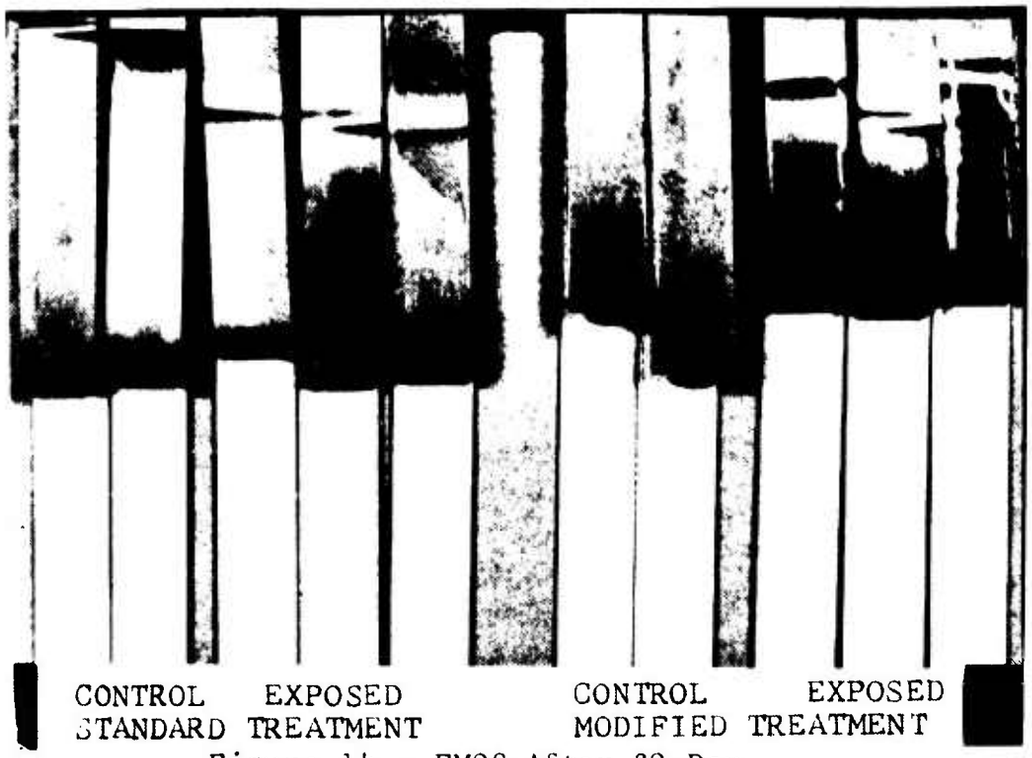

Figure 14 - FM98 After 30-Day Water Immersion

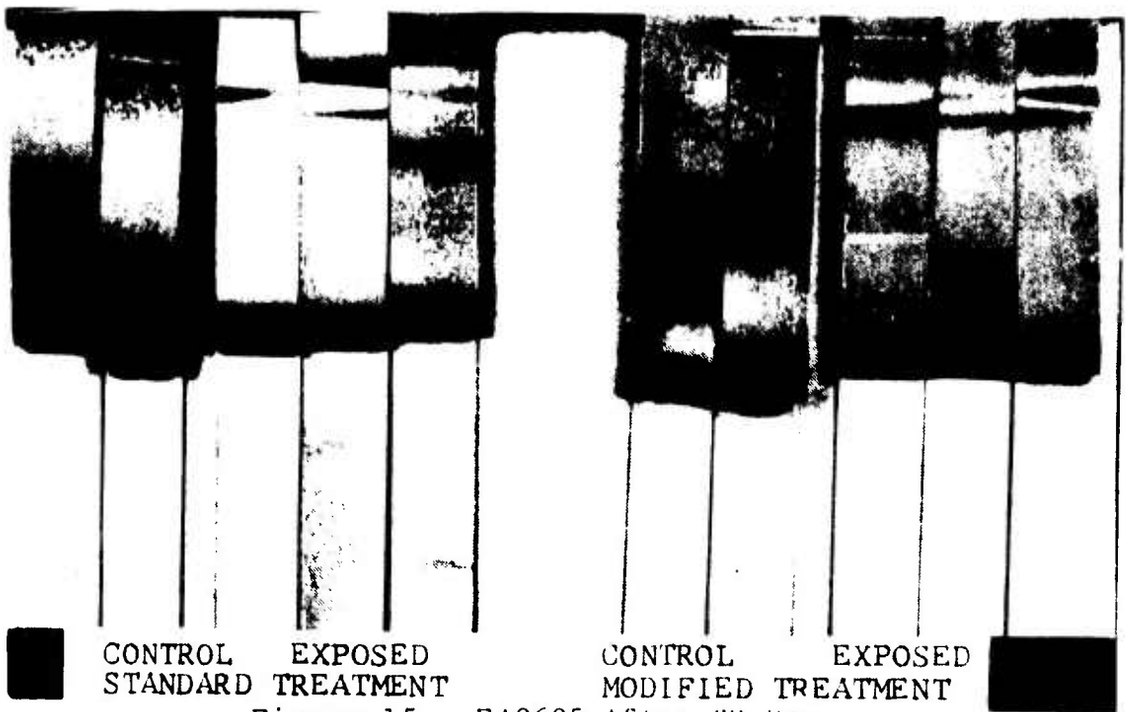

Figure 15 - EA9605 After 30-Day Water Immersion

Figure 16 - Hot Wet Creep Specimens
Installed in Test Chamber

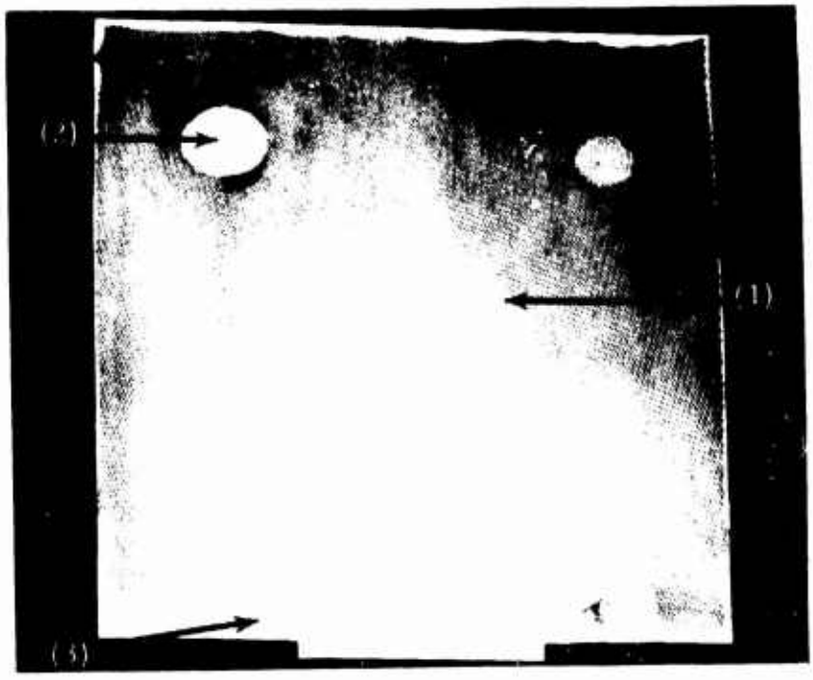

Figure 17 - Bonded Titanium Panel (Top Side)
1. Rigidized Titanium Skin
2. Honeycomb Core
3. Titanium Doubler

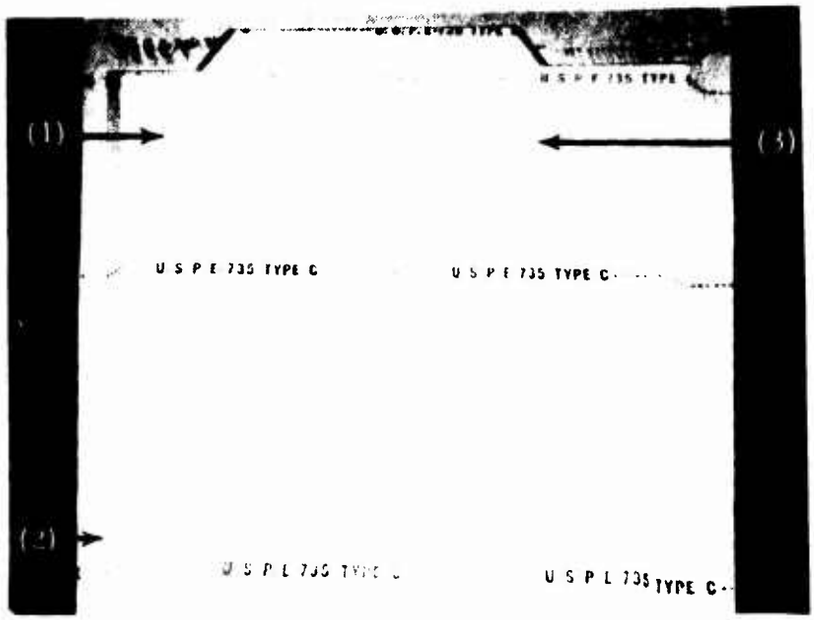

Figure 18 - Bonded Titanium Panel (Bottom Side)
1. Fiberglass Skin
2. Area of Titanium Doubler Around Periphery of Panel
3. Areas of Filled Core for Inserts

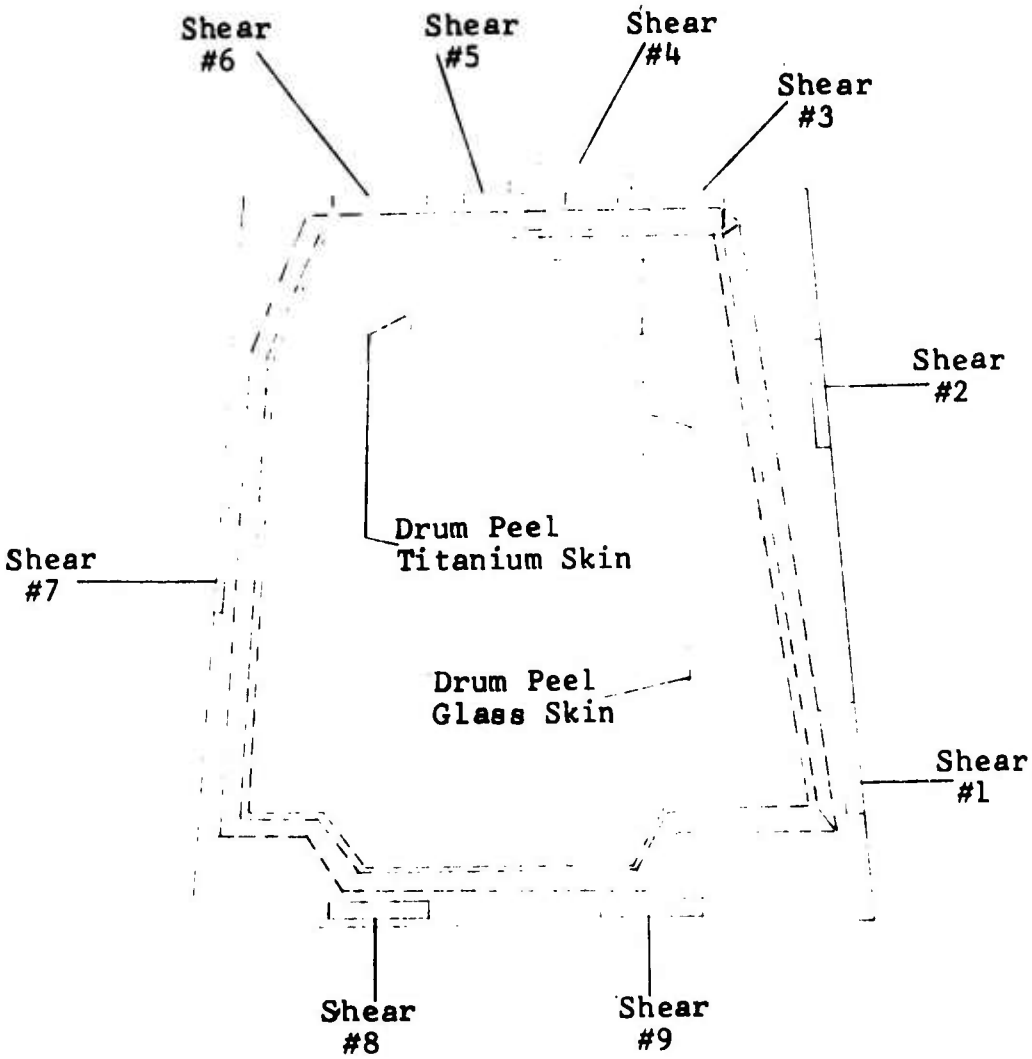

Figure 19 - Location of Destructive Test Specimens

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1. Hamilton, W. C., Lyerly, G. A., and Frohnsdorff, Jr., Picatinny Arsenal Technical Report 4362, June 1972, "Evaluation of the Adhesive Bonding Processes Used In Helicopter Manufacture, Part 3: Development of Improved Titanium Surface Treatments."

2. Wegman, R. F., Ross, M. C., Slota, S. A., and Duda, E. S., Picatinny Arsenal Technical Report 4186, September 1971, "Evaluation of the Adhesive Bonding Processes Used In Helicopter Manufacture, Part 1: Durability of Adhesive Bonds Obtained as Result of Processes Used in the UH-1 Helicopter."

3. Hamilton, W. C., and Lyerly, G. A., Picatinny Arsenal Technical Report 4185, March 1971, "Evaluation of the Adhesive Bonding Processes Used in Helicopter Manufacture, Part 2: The Characterization of Adherend Surfaces."

4. Bell Helicopter Process Specification FW 4352, "Surface Preparation of Materials for Adhesive Bonding."

5. Standard Methods for Examination of Water, Sewage and Industrial Waste, APHA, AWWA and ISIWA.